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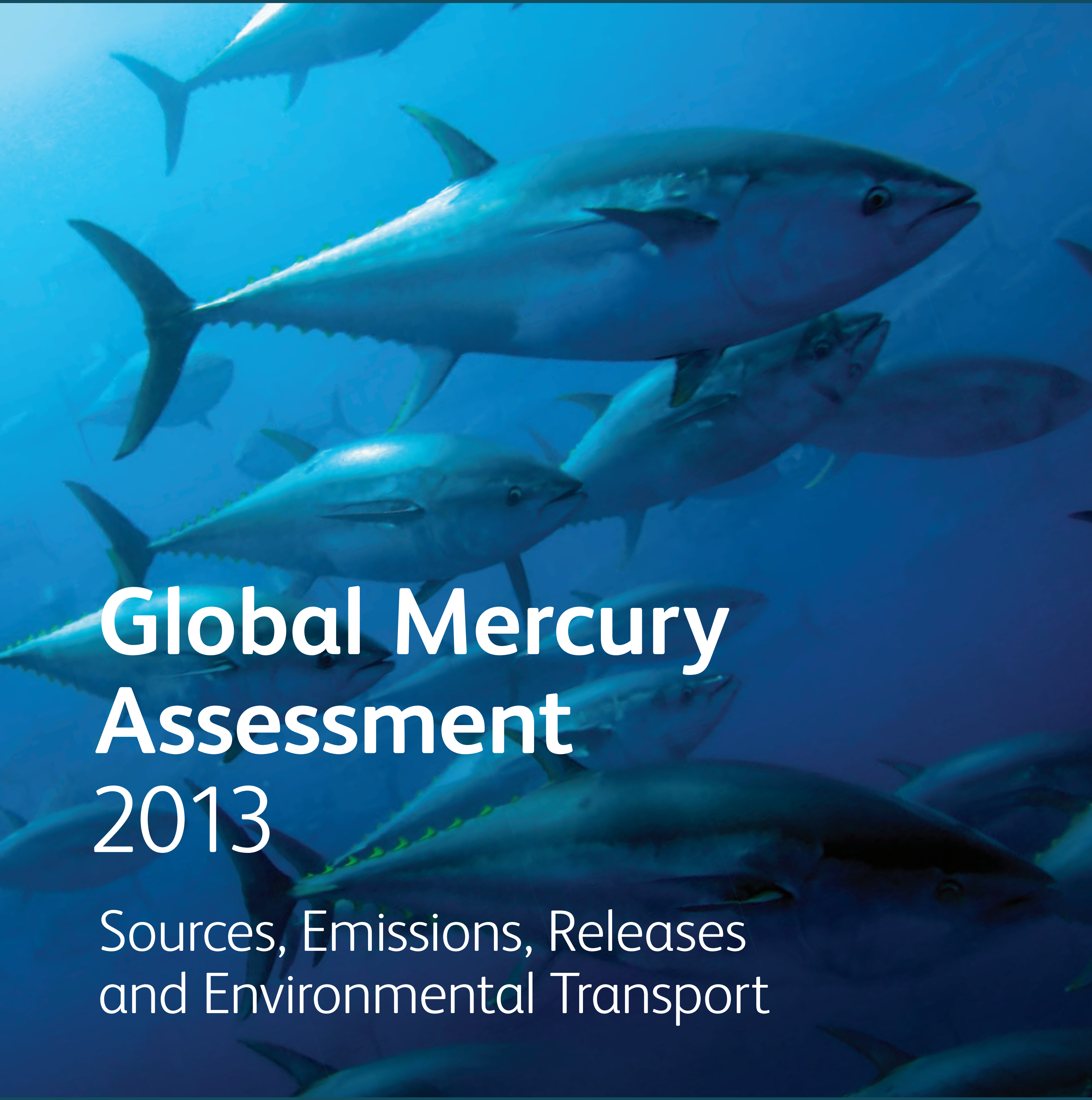

Global Mercury Assessment 2013

Sources, Emissions, Releases and Environmental Transport

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Cover photo: Tuna fish (Ugo Montaldo / Shutterstock.com). Marine food-webs are an important route of human dietary exposure to mercury.

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Executive Summary

Mercury is a global threat to human and environmental health. This report, focusing on anthropogenic emissions of mercury and their transport and transformation in the environment, is a contribution to international efforts to reduce mercury pollution.

This summary report and the accompanying Technical Background Report for the Global Mercury Assessment 2013 are developed in response to Decision 25/5, paragraph 36 of the Governing Council of the United Nations Environment Programme (UNEP), that:

Requests the Executive Director, in consultation with Governments, to update the 2008 report entitled "Global Atmospheric Mercury Assessment: Sources, Emissions and Transport," for consideration by the Governing Council/Global Ministerial Environment Forum at its twenty-seventh session.

The report provides the most recent information available on worldwide atmospheric mercury emissions, releases to the aquatic environment, and the transport and fate of mercury in the global environment. The report emphasizes emissions to air from human (anthropogenic) activities, but includes releases to water because the aquatic environment is the main route of exposure to humans and wildlife. It is in aquatic systems that the inorganic mercury is transformed into the more toxic form, methylmercury, which can accumulate in fish and marine mammals consumed by humans.

This Executive Summary presents an overview of the key findings of the Global Mercury Assessment 2013.

Total anthropogenic emissions of mercury to the atmosphere in 2010 are estimated at 1960 tonnes.[2]

The 2010 emissions inventory has several improvements over the previous inventory for 2005, including:

- A more detailed analysis of emissions from some major source sectors.
- A more detailed consideration of the mercury content of fuels and raw materials used in different countries/regions.
- New and updated information on artisanal and small-scale gold mining.
- The use of different pollution control technologies in different countries and regions have been factored into the emissions estimates.
- Emission estimates for sectors not previously included, such as aluminium production, oil refining, and contaminated sites.
- More and better information on location of major point sources such as individual power plants, smelters and cement kilns.
- Better documentation and greater transparency with respect to the data and information behind the estimates

Using this approach, the global emissions to air from anthropogenic sources is estimated as 1960 tonnes in 2010. Despite recent progress in improving the available knowledge base, the emissions estimate still has large associated uncertainties, giving a range of 1010-4070 tonnes. The work also identifies potentially important sectors that are not yet quantified, including use of mercury in vinyl-chloride monomer production; secondary metals production and ferro-alloys; oil and gas extraction and transport; and industrial and some hazardous waste incineration.

Present day anthropogenic emissions contribute to both current and future emissions to the air

Current anthropogenic sources are responsible for about 30% of annual emissions of mercury to air. Another 10% comes from natural geological sources, and the rest (60%) is from 're-emissions' of previously released mercury that has built up over decades and centuries in surface soils and oceans. Although the original source of this re-emitted mercury cannot be determined with certainty, the fact that anthropogenic emissions have been larger than natural emissions since the start of the industrial age about 200 years

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[2] 1 tonne = 1000 kilograms

ago implies that most re-emitted mercury was originally from anthropogenic sources. Reducing current anthropogenic sources is therefore vital to reduce the amount of mercury that is cycling in the environment.

Artisanal and small-scale gold mining and coal burning are the major sources of anthropogenic mercury emissions to air

The inventory confirms the role of artisanal and small-scale gold mining (ASGM) and coal burning as the largest components of anthropogenic emissions, followed by the production of ferrous and non-ferrous metals, and cement production.

Annual emissions from ASGM are estimated at 727 tonnes, making this the largest sector accounting for more than 35% of total anthropogenic emissions. This is more than twice the figure from this sector in 2005, however, most of the increase is attributed to some new and better information. For example, West Africa was thought in 2005 to have minimal ASGM activity but is now recognized as an important source region. It is thus difficult to determine whether actual emissions from this sector have changed because their estimation involves a great deal of uncertainty. Much of the activity is unregulated or even illegal, and thus reliable official data are still hard to obtain. More work is needed to confirm the emissions estimates from this sector, including field measurements around ASGM sites to better establish the amounts and fate of the mercury used.

A large amount of coal is burned around the world to generate electricity, to run industrial plants, and for in-home heating and cooking. Coal burning emitted some 475 tonnes of mercury in 2010, the majority of which is from power generation and industrial use. The estimate of emissions from other coal burning (including domestic and residential burning) is lower than that reported in the previous global assessment, due to differences in estimates of the amounts and mercury content of coal burned in these uses. Use of coal for power generation and industry is increasing, especially in Asia. However, wider use of air pollution controls and more stringent regulations in several countries, together with improved combustion efficiency, have reduced emissions from coal-burning power plants, helping to offset most of the increase arising from higher coal consumption.

Global anthropogenic mercury emissions from industrial sources may be rising.

Emissions to air are thought to have peaked in the 1970s, declined over the following two decades, and have been relatively stable between 1990 and 2005. There were some indications of slight increases in emissions between 2000 and 2005.

Any evaluation of trends needs to take into account changes in reporting and methods used to produce inventory estimates, including the introduction of additional sectors. Thus, a direct comparison of the results of global inventories produced over the past 25 years is not possible. A preliminary re-calculation, using the improved methodology, of global anthropogenic emissions in 2005 indicates that emissions from fossil fuel combustion, metal and cement production increased between 2005 and 2010, but continue to decline in other sectors such as the chlor-alkali industry. Overall, indications are that emissions from industrial sectors have increased again since 2005.

Future emission trends have been examined using scenarios and models. Without improved pollution controls or other actions to reduce mercury emissions, mercury emissions are likely to be substantially higher in 2050 than they are today.

Comparing emissions estimates reported under different reporting systems is not straightforward

The 2010 global inventory results were generally consistent with nationally reported emissions estimates for 2010, providing a degree of confidence in the methods used. However, comparing estimates for individual countries and sectors is complicated by differences in reporting methods, in particular the specification and categorisation of sectors used in different national and international reporting systems. National emissions estimates based on individual facility reporting and site measurements should be more accurate than those based on the global inventory methodology. However, this is difficult to evaluate as most nationally reported inventories lack estimation of associated uncertainties. It is also important to recognize that many measurement-based estimates are based on relatively few measurements covering short periods that are then extrapolated to produce annual emissions. It is important that all reporting is subject to validation and that associated uncertainties are quantified. If different reporting systems are to be compared, they need to be better aligned in terms of the emission sources that are identified and used.

Asia contributes almost half of global anthropogenic mercury emissions.

Increasing industrialization has made Asia the main source region of mercury emissions to air, with East and Southeast Asia accounting for about 40% of the global total, and South Asia for a further 8%. The new data on ASGM and the related increase in emission estimates from this sector have increased South America and sub-Saharan Africa's share of global emissions. However, modelling results continue to indicate that East Asia is the dominant source region for long-range airborne mercury transport worldwide.

Anthropogenic releases of mercury to water total 1000 tonnes at a minimum.

Previous UNEP global mercury assessments considered only atmospheric emissions. The 2013 report is thus the first attempt to compile a global inventory of aquatic releases. Three types of sources were considered. Point sources are industrial sites such as power plants or factories, and they release an estimated 185 tonnes of mercury per year. Contaminated sites, including old mines, landfills, and waste disposal locations, release 8 - 33 tonnes per year. Artisanal and small-scale gold mining was evaluated separately, with total releases to water and land totalling more than 800 tonnes per year. Deforestation mobilizes another 260 tonnes of mercury into rivers and lakes. Other sources remain to be quantified, and so these estimates comprise only a partial total. Thus, anthropogenic releases to waters are likely to be at least 1000 tonnes per year.

Mercury concentrations in the oceans and in marine animals have risen due to anthropogenic emissions.

Anthropogenic emissions and releases have doubled the amount of mercury in the top 100 meters of the world's oceans in the last 100 years. Concentrations in deeper waters have increased by only 10-25%, because of the slow transfer of mercury from surface waters into the deep oceans. In some species of Arctic marine animals, mercury content has increased by 12 times on average since the pre-industrial period. This increase implies that, on average, over 90% of the mercury in these marine animals today comes from anthropogenic sources. The timing of the initial stage of the increase, which started in the mid-19th century and accelerated in the early 20th century before the rise of Asian industrialization, indicates emissions from Europe, Russia and North America were probably responsible. Studies from the South China Sea suggest a similar pattern occurring there more recently, likely as a result of Asian industrialization.

Monitoring capability continues to improve, but whether this can be sustained is uncertain.

Existing mercury monitoring networks such as the European Monitoring and Evaluation Programme (EMEP), the Arctic Monitoring and Assessment Programme (AMAP), the North American Mercury Deposition Network (NAMDN), and others in the northern hemisphere have been complemented by new monitoring sites in the southern hemisphere, in particular, some sites established under the Global Mercury Observing System (GMOS) initiative. The longer-term status of many of the newly established sites however depends on availability of sustained funding to continue operations.

Anthropogenic emissions and releases over time have increased mercury loads in the environment, so the effects of reductions in emissions will often take time to become apparent.

Large amounts of mainly inorganic mercury have accumulated in the environment, in particular in surface soils and in the oceans, as a result of past emissions and releases. Owing to their larger volumes, intermediate and deep ocean waters below 100 metres actually store much larger tonnages of anthropogenic mercury than surface waters. There are also relatively large tonnages of natural mercury circulating in the intermediate and deep waters. A significant fraction of the mercury in intermediate waters is recycled back to the surface each year by upwellings. Today's anthropogenic emissions continue to load the oceans, and the catchments and sediments of lakes and rivers, with inorganic mercury. This mercury, which is the "feed-stock" for toxic methylmercury production, is stored and re-cycled in the bioavailable part of the environment for decades or centuries before it eventually is removed by natural processes. One consequence is that there will likely be a time-lag of years or decades, depending on the part of the water column, before emissions reductions begin to have a demonstrable effect on mercury levels throughout the environment and in the fish and marine mammals which are part of the human food-chain. At the same time, mercury levels in parts of the Atlantic Ocean are decreasing, likely due to reduced emissions in past decades in North America and Europe, indicating that emissions reductions can eventually lead to decreases in mercury levels in surface oceans. This reinforces the need to continue and strengthen international efforts to reduce current mercury emissions and releases, as delays in action now will inevitably lead to slower recovery of the world's ecosystems in future from mercury contamination.

Global climate change may also complicate the response of global ecosystems to mercury emission reductions, through its profound effects on many aspects of the movement and chemical transformations of mercury in the environment. For example, warmer temperatures may increase rates of organic productivity in freshwater and marine ecosystems, and rates of bacterial activity, possibly leading to faster conversion of inorganic mercury to methylmercury. Thawing of the enormous areas of northern frozen peatlands may release globally-significant amounts of long-stored mercury and organic matter into Arctic lakes, rivers and ocean.

1

Introduction

Background and mandate

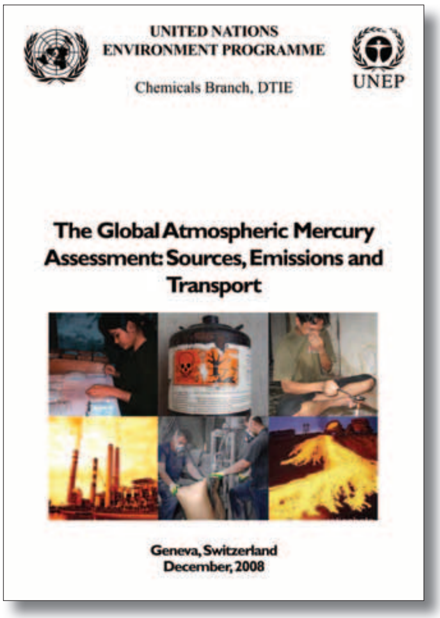
Global inventories for mercury emissions to air from human sources have been produced at approximately 5-year intervals since 1990 by scientific groups. UNEP produced its first Global Mercury Assessment in 2002. In 2007, the Governing Council of UNEP through its decision 24/3 requested the Executive Director of UNEP:

to prepare a report, drawing on, among other things, ongoing work in other forums, addressing:

(a) Best available data on mercury atmospheric emissions and trends including where possible an analysis by country, region and sector, including a consideration of factors driving such trends and applicable regulatory mechanisms;

(b) Current results from modelling on a global scale and from other information sources on the contribution of regional emissions to deposition which may result in adverse effects and the potential benefits from reducing such emissions, taking into account the efforts of the Fate and Transport partnership established under the United Nations Environment Programme mercury programme.

The results of this request were presented as a summary report entitled “The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport”, released in December 2008, and an accompanying “Technical Background Report to the Global Atmospheric Mercury Assessment”.



UNITED NATIONS
ENVIRONMENT PROGRAMME
Chemicals Branch, DTIE
UNEP

The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport

Geneva, Switzerland
December, 2008

UNEP’s 2008 Global Atmospheric Mercury Assessment Report.

The technical background report, which formed the basis for statements made in the summary report and was prepared in cooperation with the Arctic Monitoring and Assessment Programme (AMAP) Secretariat, included an updated inventory of anthropogenic emissions of mercury to the atmosphere. The inventory was based on national emissions data for the year 2005 submitted by governments, as well as estimates prepared for countries that did not provide data, and was coordinated with work related to mercury under the UN Economic Commission for Europe Convention on Long-range Transboundary Air Pollution (LRTAP). The report also drew on the work of the UNEP Global Mercury Partnership, in particular the Mercury Air Transport and Fate Research partnership area.

In 2009, the Governing Council of UNEP, through its Decision 25/5, paragraph 36, requested the Executive Director of UNEP:

… in consultation with Governments, to update the 2008 report entitled Global Atmospheric Mercury Assessment: Sources, Emissions and Transport for consideration by the Governing Council/Global Ministerial Environment Forum at its twenty-seventh session.

This updated Global Mercury Assessment 2013 and its accompanying and updated Technical Background Report are the response to that Governing Council request.

Developing the 2013 Report

As in 2008, the *Technical Background Report for the Global Mercury Assessment 2013* forms the basis for the statements made in the Summary

Report and is fully referenced according to standard scientific practice. As such, it is the single reference for the Summary Report. It has again been prepared in co-operation with the Arctic Monitoring and Assessment Programme (AMAP) and uses national data and information submitted by several governments. Contributions have also been incorporated from the UNEP Global Mercury Partnership, in particular its partnership areas on mercury control from coal combustion, reducing mercury in artisanal and small-scale gold mining (ASGM), and mercury air transport and fate; AMAP mercury expert group; UN Economic Commission for Europe (UN ECE) Long-range Transboundary Air Pollution (LRTAP) Convention groups; industry; and non-governmental organizations. Each section was prepared by a team of experts and then reviewed to ensure its scientific accuracy. The evaluation of information of mercury released into the aquatic environment benefits from contributions from the Group of Experts on Scientific Aspects of Marine Environmental Protection (GESAMP).

Scope and coverage

This update to the Global Mercury Assessment provides the most recent information available for the worldwide emissions, releases, and transport of mercury in atmospheric and aquatic environments. To the extent possible, the information comes from the published scientific literature, supplemented where necessary by other sources. Since the Global Mercury Assessment is intended as a basis for decision making, emphasis is given to anthropogenic emissions (mercury going into the atmosphere) and releases (mercury going into water and land), that is, those associated with human activities.

The Technical Background Report includes a detailed inventory of global mercury emissions to air based on data for 2010. “Inventory” in this context means a compilation of the estimated emissions and releases from various sectors and sources. While it attempts to catalogue all major sources of mercury emissions worldwide, it should not be regarded as complete and exhaustive.

In addition, for the first time, this Global Mercury Assessment includes an evaluation of information of mercury released into the aquatic environment and its associated pathways and fate. The information available for this evaluation is less complete than that for emissions to air and is based on data from recent years. The inclusion of this new element of the Global Mercury Assessment is as a response to the requests from many governments in the Intergovernmental Negotiating Committee (INC) for more information on releases to land and water. The aquatic environment is the main route of exposure to humans and wildlife, because it is in water that inorganic mercury is transformed into highly toxic methylmercury.

The Technical Background Report includes chapters on:

- *Global Emissions of Mercury to the Atmosphere*, describing sources, anthropogenic emissions, and trends in emissions;
- *Atmospheric Pathways, Transport and Fate*, examining pathways, levels and trends in air and deposition, and modelling of pathways and deposition;
- *Global Releases of Mercury to Aquatic Environments*, containing global estimates of releases to water; and
- *Aquatic Pathways, Transport and Fate*, examining mercury pathways in aquatic systems that result in important routes of human exposure.

Technical Background Report chapters were prepared by teams of experts and then reviewed to ensure their scientific validity. This Summary Report is based on the content of the Technical Background Report and has been reviewed by the authors of the Technical Background Report. It was also circulated for national review.

This Summary Report provides, in Chapter 2, an overview of natural and anthropogenic sources of mercury, outlining the main sectors involved. The global inventory of anthropogenic emissions to air is presented in Chapter 3, and Chapter 4 describes trends in mercury emissions to the atmosphere. What happens after mercury is released to the atmosphere is covered in Chapter 5 on atmospheric chemistry, monitoring, and deposition, and Chapter 6 on atmospheric concentrations and deposition. Chapter 7 provides a first attempt to estimate global releases to water, followed in Chapter 8 by a discussion of aquatic pathways, transformations, and fate. A review of gaps in knowledge is given in Chapter 9. Chapter 10 summarizes key findings.

What's new in the Global Mercury Assessment 2013

Global mercury emissions inventories continue to improve as new data and better data become available concerning some sources. The method for compiling the inventory of anthropogenic emissions to the atmosphere has also been revised and improved. Differences in air pollution control technologies and differences in the mercury content of raw materials and fuels in different countries and regions have been factored into emissions calculations to better reflect actual conditions in each country.

In the Global Mercury Assessment 2013, a new updated inventory, based on data from 2010, is presented in which some new sources (including emissions from combustion of natural gas and primary aluminium production and emissions associated with oil refining) have been quantified for the first time. A more detailed analysis has also been made of some of the major mercury emission sectors, including the break-down of emissions from coal burning in power plants, industrial and other uses. In addition, new information acquired through the UNEP Global Mercury Partnership area on Reducing Mercury in Artisanal and Small-scale Gold Mining, in particular from the Artisanal Gold Council, has resulted in a significant re-evaluation of emissions from the ASGM sector.

New observational data and new modelling results provide fresh insight into atmospheric mercury transport and fate.

One of the objectives of the updated assessment has been to provide transparent documentation and comprehensive compilations of the data that form the basis for all of the estimates presented. This approach will allow a more consistent and replicable method for compiling the global mercury emission inventory, so that valid comparisons can be made in the future. In addition, a wider range of experts from around the world have been involved in preparing the Technical Background Report on which this summary is based.

The inclusion of an assessment of releases of mercury to the aquatic environment and its subsequent pathways and fate is a further significant development as these topics were not addressed in the 2008 UNEP Global Atmospheric Mercury Assessment. The aquatic environment is critical for three reasons:

- Hundreds of tonnes of mercury is released directly into water, so an inventory limited to mercury emissions to air provides an incomplete assessment of anthropogenic impacts on the mercury cycle.
- Mercury in aquatic environments can be transformed into methylmercury, which is far more toxic to humans and animals and can enter and biomagnify in food webs more readily than other forms of mercury.
- Much human exposure to mercury is through the consumption of fish and other marine foods, making aquatic pathways the critical link to human health.

A large open artisanal and small-scale gold mining pit.

Sources of mercury emissions to air and releases to water

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Mercury is a naturally occurring element and is found throughout the world. There are thus many natural sources of mercury, creating background environmental levels that have been present since long before humans appeared.

Mercury is contained in many minerals, including cinnabar, an ore mined to produce mercury. Much of the present day demand for mercury is met by supply from mercury recovered from industrial sources and stockpiles rather than from mercury mining. Mercury is also present as an impurity in many other economically valuable minerals, in particular the non-ferrous metals, and in fossil fuels, coal in particular.

Human activity, especially mining and the burning of coal, has increased the mobilization of mercury into the environment, raising the amounts in the atmosphere, soils, fresh waters, and oceans. The majority of these human emissions and releases of mercury have occurred since 1800, associated with the industrial revolution based on coal burning, base-metal ore smelting, and gold rushes in various parts of the world. To some extent the same drivers of mercury emissions and releases are continuing with fossil-fuel-based energy generation powering industrial and economic growth in Asia and South America, which in turn helps drive high demand for metals including gold, spurring artisanal and small-scale gold mining (ASGM) around the world.

In preparing inventories of mercury emissions and releases, it is important to distinguish various categories of sources. Three main types of emissions and releases can be distinguished, each of which is briefly introduced here in qualitative terms, with particular emphasis on anthropogenic sources.

Natural sources of mercury emissions and releases

Mercury in the earth's crust can be emitted and released in several ways to air, water, and land. Natural weathering of mercury-containing rocks


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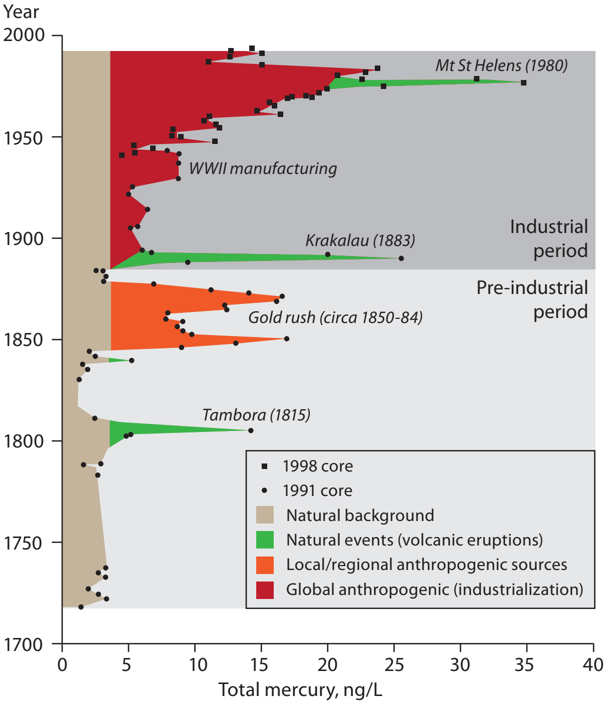
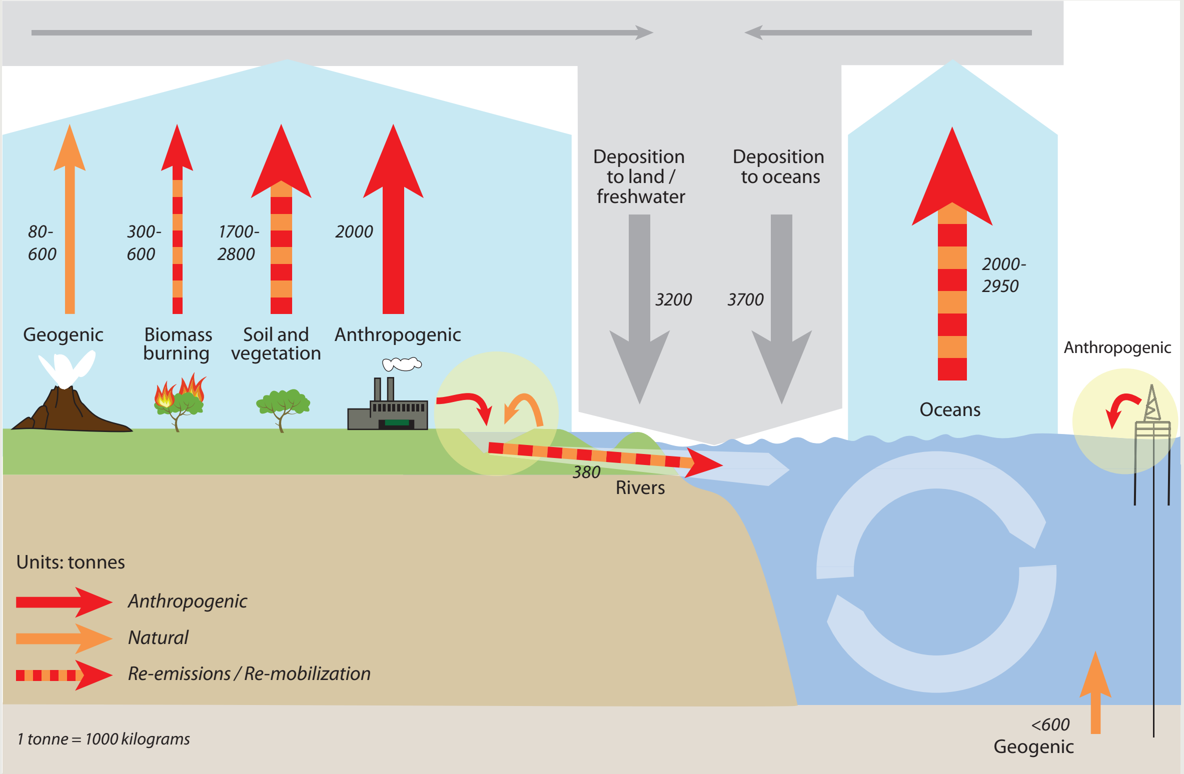
Cinnabar: the principal ore of mercury.



Ice core record of deposition from Wyoming, USA. The elevated levels associated with the 1850-84 US gold rush probably reflect local/regional sources rather than a global signature. Increasing environmental levels of mercury associated with industrialization, however, are found in environmental archives like this ice core around the globe.

Global mercury cycling

Mercury is released to the environment from natural sources and processes and as a result of human activities. Once it has entered the environment, mercury cycles between air, land, and water until it is eventually removed from the system through burial in deep ocean sediments or lake sediments and through entrapment in stable mineral compounds. Methylmercury, the most toxic and bioaccumulative form of mercury, which presents the greatest health risk to humans and wildlife, is mainly formed in aquatic environments through natural microbial processes.



Global mercury budgets, based on models, illustrate the main environmental compartments and pathways that are of importance in the global mercury cycle, and the ways in which anthropogenic releases to air land and water move between these compartments. These compartments include natural sources and anthropogenic sources, as well as re-emissions of mercury previously deposited from air onto soils, surface waters, and vegetation.

is continuous and ubiquitous, allowing mercury to escape to air and to be washed into lakes and rivers. Volcanoes emit and release mercury when they erupt. Geothermal activity can also take mercury from underground and emit it to the atmosphere and release it to the deep oceans. Some recent models of the flow of mercury through the environment suggest that natural sources account for about 10% of the estimated 5500-8900 tonnes of mercury currently being emitted and re-emitted to the atmosphere from all sources.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Anthropogenic sources of mercury emissions and releases

Anthropogenic sources of mercury emissions account for about 30% of the total amount of mercury entering the atmosphere each year.

As found in previous global mercury assessments, the main industrial sources of atmospheric mercury are coal burning, mining, industrial activities that process ores to produce various metals or process other raw materials to produce cement. In these activities, mercury is emitted because it is present as an impurity in fuels and raw materials. In these cases, mercury emissions and releases are sometimes referred to as ‘by-product’ or ‘unintentional’ emissions or releases. A second category of sources includes sectors where mercury is used intentionally. Artisanal and small-scale gold mining (ASGM) is the largest of these, in which mercury emissions and releases result from the intentional use of mercury to extract gold from rocks, soils, and sediments. Other intentional-use release sectors include waste from consumer products (including metal recycling), the chlor-alkali industry, and the production of vinyl-chloride monomer.

Coal burning, and to a lesser extent the use of other fossil fuels, is one of the most significant anthropogenic source of mercury emissions to the atmosphere. Coal does not contain high concentrations of mercury, but the combination of the large volume of coal burned and the fact that a significant portion of the mercury present in coal is emitted to the atmosphere yield large overall emissions from this sector. The mercury content of coal varies widely, introducing a high degree of uncertainty in estimating mercury emissions from coal burning. Data on mercury content is now available from many countries, including major emitters of mercury.

Mining, smelting, and production of iron and non-ferrous metals are also a large source of global mercury emissions to air, and also a very important sector with regard to releases to water. In the mining and processing of metals, most of the mercury is captured and either stockpiled or sold for use in various products, creating anthropogenic sources associated with intentional use, discussed below. Nonetheless, the volume of ores and metals involved result in large total emissions and releases. The relatively small volume of primary mercury production makes mercury mining a far smaller source today than it has been in the past.

Cement production, which typically involves the burning of fossil fuels to heat the materials required to make cement, is another major anthropogenic source of mercury emissions. Both the raw materials and the fuel may contain mercury and lead to emissions. The amount of mercury involved varies greatly with the mercury content of these fuels and especially with the raw materials. In some countries, cement kilns are burning increasing amounts of alternative fuels, including wastes that may contain mercury. This may add to the emissions from cement kilns.

Oil refining emits and releases mercury, as oil deposits are known to contain mercury, generally at low concentrations. Mercury is removed from most petroleum products and natural gas prior to combustion, and therefore combustion-related emissions are low. Most of the mercury in crude oil is associated with solid waste that is disposed of in landfills. However, emissions and releases during refining of crude oil do occur and these have been quantified for the first time in the 2010 inventory. The inventory does not quantify other emissions and releases during oil and gas extraction and transport or from flaring.

Unintentional mercury emissions from these sectors can be reduced by the application of pollution control measures at power plants and industrial plants. Some of the mercury captured is refined and enters the commercial supply chain; however, large amounts of mercury captured in materials such as fly ash and oil refinery waste need to be disposed of. Some of the resulting wastes are themselves used as raw materials, for example in construction materials, but large amounts are disposed of in landfills, which can thus become a potential source of mercury emissions and releases.

Among intentional-use sectors, **Artisanal and small-scale gold mining** is a major source for emissions and releases of mercury worldwide. In ASGM, miners use mercury to create an amalgam separating gold from other materials. They then have to separate the mercury from the gold. Calculating emissions from this sector presents a particular challenge because it is typically widely dispersed and often unregulated and may be illegal. Uncertainties regarding release estimates from the ASGM sector are therefore high. Furthermore, the miners are typically poor and perhaps have little awareness of the hazards of mercury, and pollution control devices may be hard to obtain.

Wastes from consumer products containing mercury can end up in landfills or incinerators.

Mercury is still used in a wide range of products, including batteries, paints, switches, electrical and electronic devices, thermometers, blood-pressure gauges, fluorescent and energy-saving lamps, pesticides, fungicides, medicines, and cosmetics. Once used, many of the products and the mercury they contain enter waste streams. While mercury in landfills may slowly become re-mobilized to the environment, waste that is incinerated can be a major source of atmospheric mercury, especially from uncontrolled incineration. Incinerators with state-of-the-art controls have low emissions.

Another use of mercury is in **dental amalgam** for filling teeth. When bodies are cremated, mercury in fillings can be emitted. Mercury can also be emitted and released during production and preparation of fillings and from the disposal or removed fillings. In addition, mercury from removed fillings can be recycled or go into solid waste and wastewater.

The amount of mercury released in the recycling of scrap metals, for example in secondary steel and non-ferrous metal production, is generally assumed to be much lower than that released during primary metal production, which is why the present global inventory only addresses primary metal production. However, lower emissions from recycling may not be the case in all countries. Much of the scrap steel in some countries comes from automobiles that may still have devices that contain mercury, and which may not be removed prior to recycling of the steel. These devices are largely being phased out so mercury emissions from scrap steel may be expected to decrease. However, large differences exist between countries in the way they treat their mercury-containing wastes, including scrap metals that are recycled in secondary metal production.

Mercury is also used in a number of industrial processes. A major industrial use is in the **chlor-alkali industry** where mercury-cell technology may be used in the production of chlorine and caustic soda.

Mercury is also used as a catalyst in the production of **vinyl chloride monomer** (VCM) from acetylene, mainly in China.

Mercury releases to aquatic systems as a result of current human activities arise from many of the same uses or the presence of mercury in various products and processes that emit mercury to the air. As with emissions to the atmosphere, aquatic releases come from two main sources. First, mercury is released with water effluent from the sites where mercury is used. Second, mercury can leach into water from disposal sites that have mercury in the waste.

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Anthropogenic sources of mercury from industry and intentional use.

Re-emission and re-mobilization of mercury

Re-emissions constitute the third category of sources, presently comprising about 60% of mercury emissions to air. Mercury previously deposited from air onto soils, surface waters, and vegetation from past emissions can be emitted back to the air. Re-emission is a result of natural processes that convert inorganic and organic forms of mercury to elemental mercury, which is volatile and therefore readily returns to the air. Mercury deposited to plant surfaces can be re-emitted during forest fires or biomass burning. Mercury may be deposited and re-emitted many times as it cycles through the environment.

It is important that re-emitted mercury should not be considered a natural source. It may originally have come from natural or anthropogenic sources, but by the time it is re-emitted, it is difficult or impossible to identify its specific origin. Nonetheless, human activity has increased the environmental burden of mercury, resulting in higher levels of re-emission. This is compounded by changes in land use practices as well as increasing temperatures due to climate change.

In the aquatic environment, re-mobilization of mercury occurs when mercury deposited on and accumulated in soils or sediments is re-mobilized by, for example, rain or floods that cause the mercury to enter or re-enter the aquatic system. Resuspension of aquatic sediments due to wave action or storm events is an additional way for mercury to re-enter the aquatic ecosystems.

Estimating re-emission and re-mobilization rates is difficult. It is often done using modelling approaches. These models are based on data on atmospheric levels and other observations as well as current understanding of chemical transformations and other processes that determine how mercury moves between air, land, and water. The models aim to balance the amount of mercury in circulation at any given time while remaining consistent with observational data. Temperature is a key factor. With lower temperatures, re-emission rates are generally lower.

Re-emission is also a major factor in determining the length of time needed for anthropogenic emission reductions to be reflected in decreasing environmental levels of mercury. Mercury emitted in one year may be deposited to and retained in soils and waters for some time before being re-emitted or re-mobilized in subsequent years. This cycle can be repeated, keeping levels in air and water elevated even after anthropogenic sources have been lowered. Conversely, continuing to add to the global pool will leave an ever-longer legacy of anthropogenic mercury contamination worldwide. It is thus imperative that international efforts to reduce mercury emissions continue and are strengthened as soon as possible.

Arnold John Labrentz / Shutterstock.com

Forest fires re-emit mercury deposited to vegetation.

Anthropogenic emissions to the atmosphere

3

Global emissions inventory

The global emissions inventory for 2010 estimates that 1960 tonnes of mercury was emitted to the atmosphere as a direct result of human activity. The leading sectors remain the same as those identified in the 2005 inventory. Improved data, however, have changed the relative contributions of some of these sectors, as have some actual changes in emissions. All coal burning emissions taken together, for example, represent a lower percentage of the total emissions than in the 2005 inventory. This is due in part to the increased estimates from artisanal and small-scale gold mining (ASGM), and in part to much lower estimates for domestic use of coal. When the actual amount of mercury emitted from coal combustions in power generation and industrial uses is considered, and the estimates are based on the same 2010 methodology, the emissions in 2010 are the same and perhaps slightly higher than in 2005. Even though new coal-fired power plants are being built, combustion efficiency and emissions controls are also improving in most parts of the world.

Results by selected sector

The updated inventory of emissions to air confirms **coal burning** as a continuing major source of emissions, responsible for some 475 tonnes of mercury emissions to air annually, compared with around 10 tonnes from combustion of other fossil fuels. According to the new inventory, more than 85% of these emissions are from coal burning in power generation and industrial uses. In the previous assessment, emissions from domestic and residential coal burning were highlighted as a possible larger contribution. Better information on coal consumption for domestic and residential uses indicates that these activities are a smaller contribution to total emissions from coal burning than previously thought.

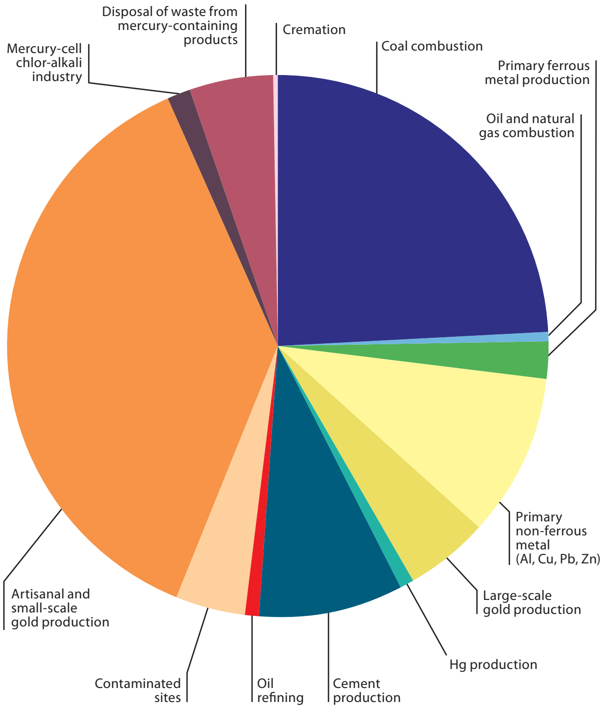
Emissions from the **cement production** industry are largely dependent on the fuels used. The new

*Emissions from various sectors, in tonnes per year with the range of the estimate, and as a percentage of total anthropogenic emissions. **Note:** These numbers cannot be compared directly with those presented in the 2008 assessment (see Chapter 4, Trends in mercury emissions to the atmosphere).*

Sector	**Emission (range), tonnes***	**%****
By-product or unintentional emissions		
Fossil fuel burning		
Coal burning (all uses)	474 (304 - 678)	24
Oil and natural gas burning	9.9 (4.5 – 16.3)	1
Mining, smelting, & production of metals		
Primary production of ferrous metals	45.5 (20.5 – 241)	2
Primary production of non-ferrous metals (Al, Cu, Pb, Zn)	193 (82 – 660)	10
Large-scale gold production	97.3 (0.7 – 247)	5
Mine production of mercury	11.7 (6.9 – 17.8)	<1
Cement production	173 (65.5 - 646)	9
Oil refining	16 (7.3 - 26.4)	1
Contaminated sites	82.5 (70 - 95)	4
Intentional uses		
Artisanal and small-scale gold mining	727 (410 – 1040)	37
Chlor-alkali industry	28.4 (10.2 – 54.7)	1
Consumer product waste	95.6 (23.7 – 330)	5
Cremation (dental amalgam)	3.6 (0.9 - 11.9)	<1
Grand Total	**1960 (1010 – 4070)**	**100**

** Values rounded to 3 significant figures.*
*** To nearest percent*

Sectors for which emissions are not currently quantified
biofuel production and combustion
vinyl-chloride monomer production, emissions during
secondary metals production and ferro-alloys
oil and gas extraction, transport and processing other than refinery emissions
industrial / some hazardous waste incineration and disposal
sewage sludge incineration
preparation of dental amalgam fillings and disposal of removed fillings containing mercury



Relative contributions to estimated emissions to air from anthropogenic sources in 2010.

inventory avoids double counting of emissions from conventional fuels (such as coal and oil) which are included under the industrial fossil fuel burning emissions. However, it does attempt to account for emissions from other fuels, including alternative fuels (such as old tyres and other wastes) and from raw materials. Increasing amounts of waste are being co-incinerated in the cement industry both as fuel but also, in some plants, as a means of disposing of hazardous wastes, some of which may contain mercury. In some regions, additional measures are being introduced to make sure that mercury emissions associated with waste co-incineration do not increase overall emissions from cement plants.

Increased application of air pollution control devices, including some mercury-specific technologies, together with more stringent regulations in several countries have the effect of reducing mercury emissions from coal burning sectors and thus offset some part of the emissions arising from increased activity.

Artisanal and small-scale gold mining emissions are, in the 2010 inventory, the major source of emissions to air, at 727 tonnes per year. The reasons for the large increase in the estimate compared to 2005 are discussed below. The global estimate for emissions from ASGM includes a significant contribution from China, although recent information on this sector in China is lacking. China prohibited ASGM in 1996 and therefore records no emissions from this sector.

Mercury-cell technology is becoming less common in the **chlor-alkali industry** as other, more cost-effective processes are adopted. No new plants are being constructed, though many older plants remain to be converted. Old chlor-alkali plants and other decommissioned industrial sites may constitute contaminated sites that continue to release mercury to the environment for many years and emissions from contaminated sites are now part of the inventory.

Global emissions from use of mercury in **dental amalgam** resulting from cremation of human remains are estimated at 3.6 (0.9 – 11.9) tonnes in 2010. Some 340 tonnes of mercury is used per year in dentistry, of which about 70-100 tonnes (i.e. 20-30%) likely enters the solid waste stream.

In the production of **vinyl chloride monomer**, information is still lacking on the lifecycle and eventual fate of the mercury catalyst. Most of this production occurs in China, and about 800 tonnes of mercury is thought to have been used by this industry in China in 2012. Used mercury catalyst is recycled and reused by enterprises that hold permits for hazardous waste management. The amounts that may be emitted or released are unknown.


Ronald de Hommel

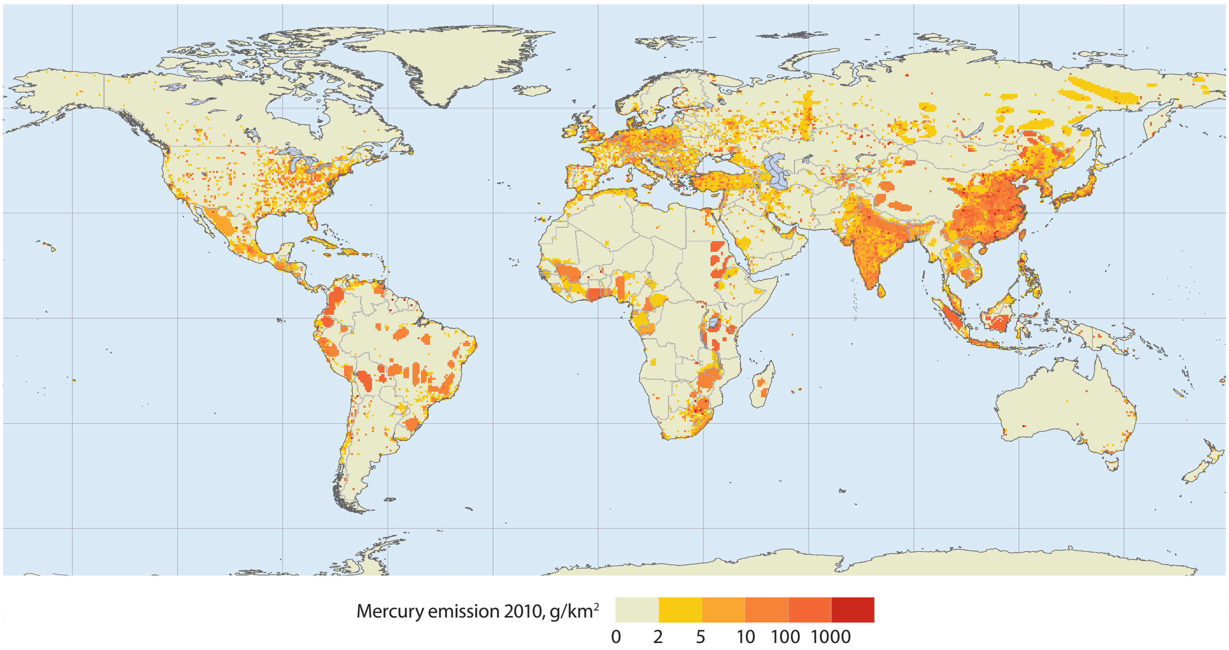
Artisanal and small-scale gold mining. Unlike most small-scale gold miners, the green gold miners of Oro Verde, shown here, employ an environmental way of mining gold that does not use mercury or other chemicals.

Results by region

The greatest proportion of anthropogenic mercury emissions to the atmosphere comes from Asia, which contributes about 50% of the global total. The majority of Asian emissions come from East and Southeast Asia. China accounts for three-quarters of East and Southeast Asian emissions, or about one third of the global total.

New data on emissions from ASGM have increased the proportion of global emissions attributed to South America and Sub-Saharan Africa, largely due to increased estimates associated with improved information about ASGM activities in these areas.

Emissions to air from other major source sectors are higher in Europe, North America, and Oceania.

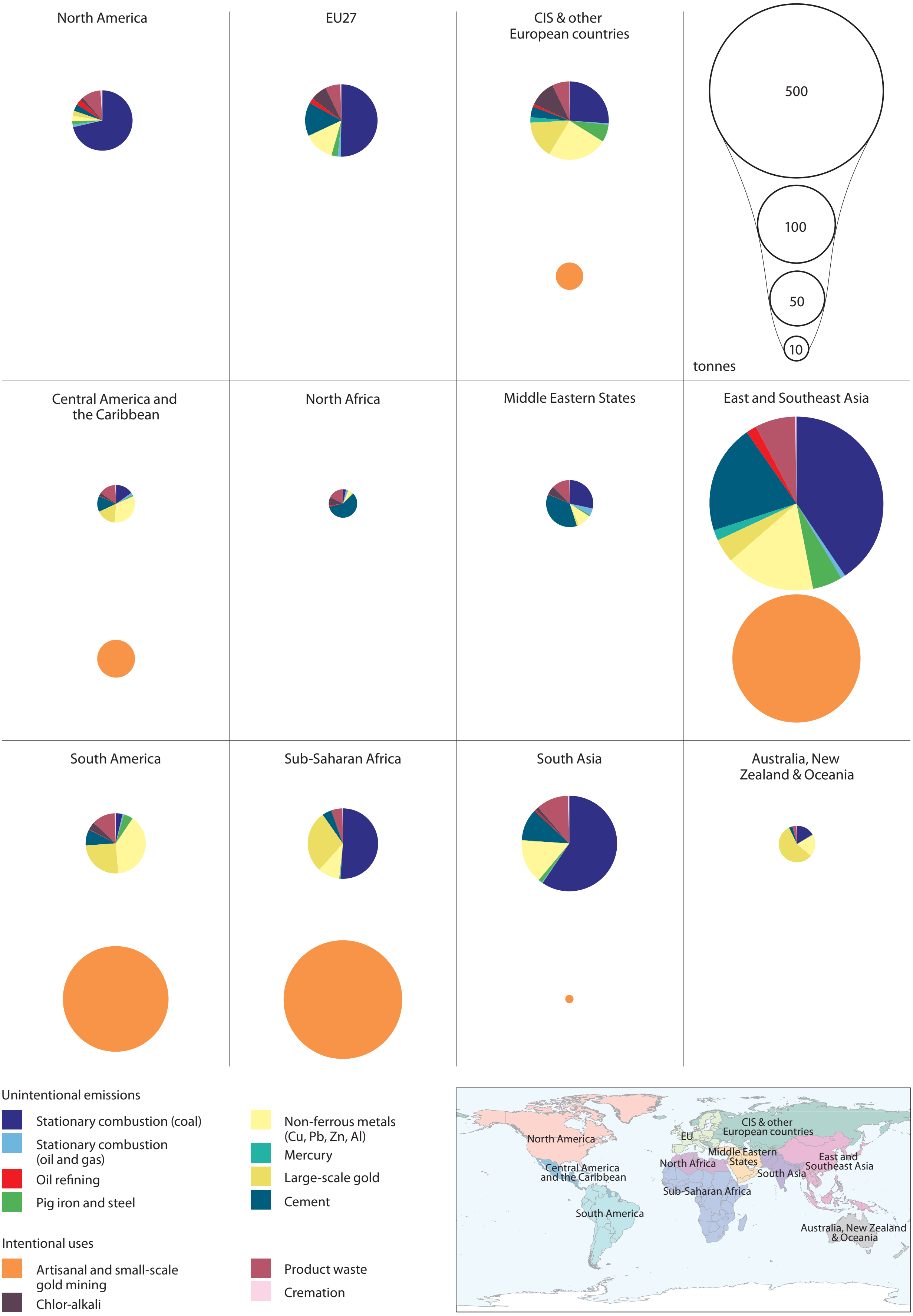


Global distribution of anthropogenic mercury emissions to air in 2010.

Emissions from various regions, in tonnes per year with the range of the estimate, and as a percentage of total global anthropogenic emissions. ***Note:*** *These numbers cannot be compared directly with those presented in the 2008 assessment (see Chapter 4, Trends in mercury emissions to the atmosphere).*

Region*	**Emission (range), tonnes****	**%**
Australia, New Zealand & Oceania	22.3 (5.4 - 52.7)	1.1
Central America and the Caribbean	47.2 (19.7 - 97.4)	2.4
CIS & other European countries	115 (42.6 - 289)	5.9
East and Southeast Asia	777 (395 - 1690)	39.7
European Union (EU27)	87.5 (44.5 - 226)	4.5
Middle Eastern States	37.0 (16.1 - 106)	1.9
North Africa	13.6 (4.8 - 41.2)	0.7
North America	60.7 (34.3 - 139)	3.1
South America	245 (128 - 465)	12.5
South Asia	154 (78.2 - 358)	7.9
Sub-Saharan Africa	316 (168 - 514)	16.1
Undefined (global total for emissions from contaminated sites)	82.5 (70.0 - 95.0)	4.2
Grand Total	**1960 (1010 – 4070)**	**100**

* See figure on the following page for map with specification of regions.
**Values rounded to 3 significant figures.



Estimates of 2010 anthropogenic mercury emissions to air from different main sectors in different regions. ASGM is shown separately to highlight its geographic distribution and better allow regional comparisons to be made for other sectors.

Compiling the 2010 inventory of anthropogenic mercury emissions to air

The inventories used in successive Global Mercury Assessments continue to improve as better data become available. The 2013 update presents an inventory of emissions for 2010 that has a number of improvements over the 2008 assessment and its inventory for 2005:

- A more detailed analysis of emissions from some major source sectors. For example, fossil fuel consumption is now broken down into categories for combustion in power plants, industry, and other uses. The type of coal or oil used is also considered, providing a more accurate estimate of mercury emissions.
- A more detailed consideration of the mercury content of fuels and raw materials used in different countries and regions.
- New and updated information on ASGM.
- The use of different pollution control technologies in different countries and regions have been factored into the emissions estimate.
- Emission estimates for sectors not previously included, such as aluminium production, oil refining, and contaminated sites.
- More and better information on location of major point sources such as individual power plants, smelters and cement kilns.
- New and updated information on ASGM.
- Emission estimates for sectors not previously included, such as aluminium production, oil refining, and contaminated sites.
- Better documentation and greater transparency with respect to the data and information behind the estimates.

The methods for estimating emissions from industrial sectors is complemented by other methods used for more dispersed emissions sources. For example, estimating emissions from some intentional-use sectors requires intensive work with those sectors. Relevant and accurate information about ASGM is generally not available through official channels. Estimating mercury emissions from its intentional use in lighting, batteries, and other products requires analysing the entire production, use, and waste stream to determine where mercury is likely to be released and in what quantities. The approach used in the 2013 assessment addresses the emissions from breakages and wastes resulting from use of these mercury-containing products in society, the majority of which are incinerated or end up in landfills. It does not, however, address industrial wastes or sewage sludge incineration.

Uncertainties in emission estimates

Estimates of mercury emissions are just that: estimates. To compile a global assessment requires making a number of assumptions and generalizations. Uncertainty associated with the 2010 inventory arises from each of the factors used to estimate the emissions: the correctness of the activity data, the validity of the emission factors applied, and the validity of assumptions regarding the effectiveness and use of emission-control technologies.

Based on an evaluation of these sources of uncertainty and the relative contributions of sectors with reliable information and those with less reliable data, uncertainty in the 2010 inventory assessment of total anthropogenic mercury emissions to air gives a range of emissions from 1010-4070 tonnes. This range is greater than that reported in some previous assessments, reflecting a greater appreciation of the sources of uncertainty due to the improved estimation methods and perhaps a more realistic appraisal of the state of knowledge concerning some aspects of emissions.

The best estimate, taking a conservative approach, is 1960 tonnes. If nationally produced estimates for 2010 available from some countries (Canada, Japan, Korea, Mexico, the United States and European countries reporting to LRTAP) are introduced into the global inventory in place of the inventory estimates, the corresponding estimated total global anthropogenic emission to air is 1940 tonnes. As most national inventories do not include uncertainty ranges, it is not possible to assign a range to this number. The recognition of uncertainties is an important consideration and presenting single national estimates can convey a misleading picture of what is known and, more importantly, not known about emissions.

The numbers derived using the methods employed to produce the global inventory for 2010 were

Methods for estimating emissions

All global mercury emissions inventories to date have used the same basic approach for the major sectors emitting mercury to the atmosphere. For specific emission sectors, national emissions estimates are calculated by multiplying the amount of activity (i.e. amounts of fuels burned, raw materials consumed, or materials produced) by an emission factor that is an estimate of the mercury emitted per unit of activity. For example, emissions from coal-fired power generation are estimated by multiplying the tonnes of coal used by the amount of mercury estimated to be released per tonne of coal. In most such inventories, "abated" emission factors have been employed to quantify both the emissions of mercury that occur during the processes and the effects of mercury emission controls. In the new methodology used to develop the 2013 report these components are split. "Unabated" emission factors are employed to quantify the emissions, and "technology profiles" have been developed to represent the effects of mercury emission controls.

Various methods are employed to estimate emissions of mercury at individual sources and at national, regional and global levels. In general, the methods fall under one of two main categories:

- Mass-balance/substance-flow based estimates, which are based on the principle that what goes in must come out. Amounts of mercury in fuels and raw materials constitute the inputs; and the outputs are the amounts of mercury emitted to air, released to water or land, retained in products or in wastes, or otherwise recovered and stored or disposed of.
- Measurement-based estimates, which rely on measurements made at appropriate points in the industrial process or in the product/waste output streams. These measurements are used to estimate where the mercury goes, as in the method above.

In principle the two approaches should produce the same results. In practice, mass-balance based approaches tend to result in higher emission estimates than most measurement-based estimates. Since future emissions reporting is likely to involve a combination of these two approaches, further work is required to understand why results may differ and to reconcile the two approaches.

Since the 2008 UNEP assessment was produced, the number of direct measurements of emissions from certain point sources (in particular power plants and some metal and cement production plants and waste incineration facilities) has increased considerably, resulting in a much improved knowledge base.

A number of countries require regular reporting of emissions. Increasing use is being made in these reporting systems of measurement-based estimates and facility-level reporting, in particular for major point sources. In other countries, national mercury emissions are only being quantified for the first time. Since 2005 and the start of the UNEP negotiating process in 2010, many countries have initiated work on national emission inventories which, in several cases, have yielded much improved information on activity data, sector characteristics and mercury emissions. Such inventories often make use of the UNEP Toolkit for identification and quantification of mercury emissions.

compared with a number of national inventories and emissions reported under other systems covering the same period. In general, the level of agreement was good, in particular when the significant uncertainties involved in both global and national estimates are taken into account. It is important to note that there are good reasons why estimates of mercury emissions produced in the 2010 inventory may not fully agree with national inventories made by countries using other methodologies. These reasons include:

- Reporting schemes may define and distinguish emissions source sectors in very different ways, and aligning these sectors may not be possible.
- Industry reporting to national government may be limited to sources with emissions above a certain threshold level so that emissions from smaller sources, below the threshold, are not reported. Where smaller sources make up a significant part of the source category, reported inventories may therefore significantly underestimate total mercury emissions.
- National inventories in some countries are making increasing use of actual measurements of mercury emissions at individual facilities. At the global scale it is not yet feasible to base an inventory on individual site emissions. Furthermore, actual measurements of mercury emissions at a source may be taken only a few times during a year and may not be fully representative of normal operations. In the 2013 assessment, a mass-balance based approach was employed to be consistent, transparent, and replicable.
- National reporting and monitoring schemes may provide information that is not available to externally produced inventories.

Despite these considerations, most of the discrepancies noted between the 2010 inventory mass-balance-based estimates and national estimates based on measurement- approaches are modest and within the margins of error associated with the different approaches. In cases where the differences are larger, it is important to recognize that there are sources of error in all methods for estimating mercury emissions.


Gunnar Futsæter

Sampling of mercury emissions at the Kendal coal-fired power plant in South Africa, conducted under a UNEP project. A probe with mercury traps is inserted into a sampling port in the stack to collect mercury present in the flue gas. The mercury traps are subsequently analysed according to the US EPA Mercury Monitoring Toolkit sampling protocol.

4

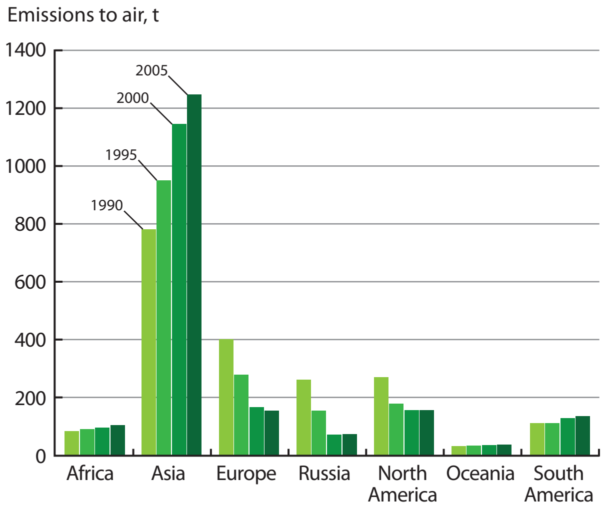
Trends in mercury emissions to the atmosphere

Assessing global and sectoral trends

A key question in assessing anthropogenic mercury emissions worldwide is whether they are increasing or decreasing. While it is tempting simply to compare the 2010 inventory with its 2005 counterpart, the results would mean little. As inventory methods develop and as additional sources are considered, the estimate of total anthropogenic mercury emissions worldwide also changes. While some changes reflect real trends, others reflect changes in methods or scope. Thus, comparing the results of previous assessments with the present update requires considerable care and involves an understanding of the way in which these inventories have been produced and the uncertainties associated with them.

It is possible, however, to compare certain sectors over time by attempting to compensate for any methodological changes between the various inventories since 1990.

Emissions to air are thought to have peaked in the 1970s. From 1990 to 2005, total anthropogenic emissions of mercury to the atmosphere appear to have been relatively stable, with decreases in Europe and North America being offset by increases in Asia. A reanalysis of the available inventories since 1990 however, indicates that emissions from industrial sectors at least may be starting to increase again.



Estimates of annual anthropogenic mercury emissions from different continents/regions, 1990-2005.

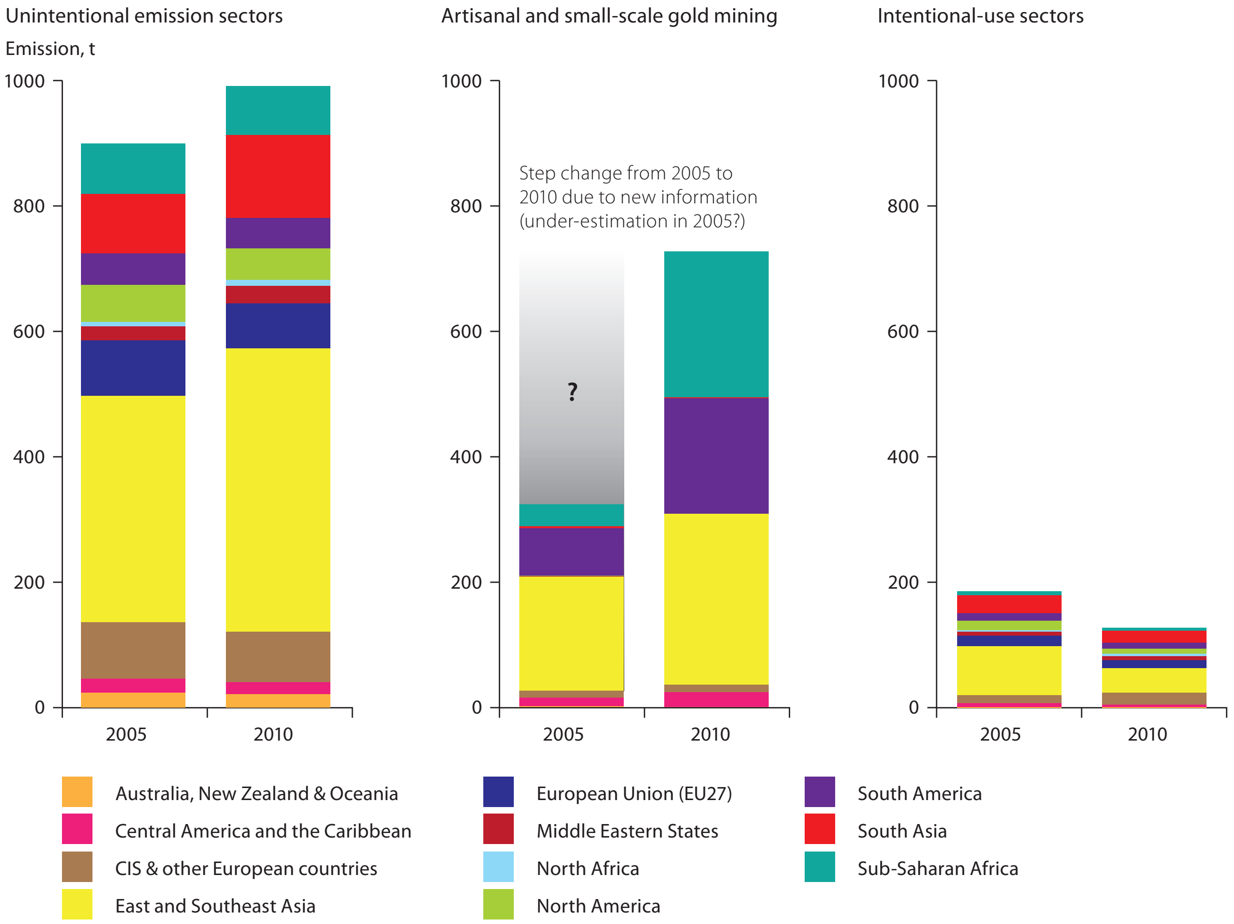
The changes introduced in the 2010 inventory methodology prevent a straight-forward continuation of this analysis. However, an evaluation of trends for some sectors between 2005 and 2010 has been made by applying the new methodology to activity data for 2005. This comparison suggests a further slight increase in the combined amount of mercury emitted by industrial sectors (coal combustion, production of cement, pig iron and steel, and non-ferrous metals). The following paragraphs describe the trend results for three sectors, to illustrate some of the developments between 2005 and 2010, and some of the the difficulties in comparing emissions estimates between different years, made with different methods.

Coal burning for power generation and for industrial purposes continues to increase, especially in Asia. However increases in the application of air pollution controls, including some mercury specific technologies, together with more stringent regulations in a number of countries have reduced mercury emissions from coal burning in power plants in particular, and thus offset some part of the emissions arising from increased coal consumption.

In the United States, for example, emissions from coal burning at power plants have reportedly decreased from about 53 tonnes in 2005 to 27 tonnes in 2010. This decrease is largely due to new regulations that have resulted in changes in the sources of the coal that is burned in large power plants and the installation of mercury controls as well as controls on sulphur dioxide and particulates that have the co-benefit of further reducing mercury emissions.

In China, many of the new coal-fired power plants have state-of-the-art pollution controls installed.

Emissions of mercury from **artisanal and small-scale gold mining** (ASGM) reported for 2010 are more than twice those reported for 2005. While the



Unintentional emission sectors: Coal burning, ferrous- and non-ferrous (Au, Cu, Hg, Pb, Zn) metal production, cement production. Intentional-use sectors: Disposal and incineration of product waste, cremation emissions, chlor-alkali industry.

Comparison of emissions in 2005 and 2010, by selected sector and region.

rise in the price of gold (from USD 400 per ounce in 2005 to USD 1100 per ounce in 2010), along with increased rural poverty, may indeed have caused more activity in this sector, the increased estimate for mercury emissions is considered to be due primarily to some more and better data from many countries and regions. West Africa, for example, was regarded as having minimal ASGM in 2005, but is now recognized as a region with considerable activity. Thus, the baseline has improved, without necessarily any change in actual activity or emission levels.

Waste from consumer products is affected by the amount of mercury used. For most products in which mercury is used, mercury-free alternatives exist. Consequently, many of these uses of mercury are declining, at least in some regions, as alternative products or processes are adopted. Compact fluorescent light bulbs are an exception. Even though the mercury content of individual light bulbs has decreased, use of this type of light bulb is increasing rapidly.

In order to make valid assessments of trends in emissions from global inventories, comparable data on activity levels are required, together with information on changes in fuel and raw material characteristics and applied air pollution control technology. One aim of the 2010 inventory methods is to create a firmer foundation for such future trend analysis.


Ralf Siemieniec / Shutterstock.com

Use of mercury-containing energy-saving lamps is increasing.

Emission scenarios and future trends

The 2008 *Global Atmospheric Mercury Assessment* included a first attempt at projecting future emissions inventories. These were based on three scenarios: continuing with the status quo, applying current emissions controls worldwide, and achieving maximum feasible technological reductions. At the time, this effort was regarded as highly provisional. Since then, additional studies have extended and improved this work, but the results are not markedly different from earlier projections of future mercury emissions.

Global mercury models have been used to evaluate future scenarios. Four global and hemispheric models projected mercury levels around the world in 2020, based on the three emission scenarios described earlier. In industrial regions, the status quo will cause an increase in mercury levels of 2-25%, and in remote areas of 1.5-5%. The two emission control scenarios, on the other hand, yield a decrease in mercury in industrial areas of 25-35%, and in remote areas of 15-20%.

Another global model was coupled with estimates of surface reservoirs of mercury in order to quantify source-receptor relationships for the present and for 2050. Under the best-case scenario of maximum feasible reductions, projected estimates for deposition in 2050 is similar to estimates for today. In the other scenarios, increasing emissions lead to increasing deposition. A greater proportion of mercury emissions is expected to be in the oxidized form, so that a greater proportion will be deposited near the source instead of being transported far away.

The model results support the conclusion that reducing anthropogenic emissions will slowly reduce the amount of mercury in biologically available reservoirs. Over time, mercury in the environment will be taken out of circulation by natural processes, for example from ocean waters down into sediments, and biologically available mercury will decrease. Increased emissions, on the other hand, will continue to build up the amount of mercury in circulation.

With new databases and methods, it may soon be possible to create scenarios that incorporate activity levels as well as technology use for each country. If this were done, it would allow countries to assess the effects of different mercury reduction strategies on their national emissions. For example, a country could determine the relative contributions of emission reduction technology as opposed to, for example, changes in raw materials.

Atmospheric chemistry, monitoring, and trends

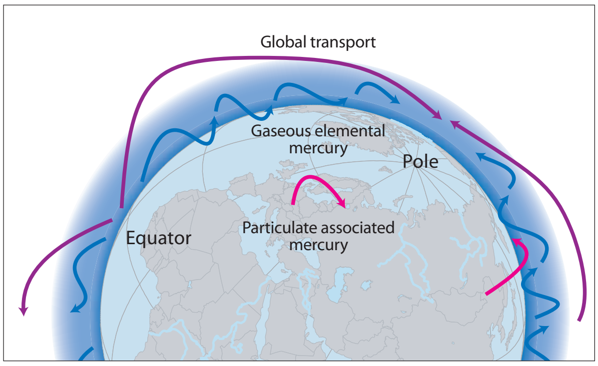
5

Forms of mercury in air

Mercury in the atmosphere is in three primary forms. Gaseous elemental mercury is the most common in anthropogenic and natural emissions to the atmosphere. Gaseous oxidized mercury and mercury bound to particulates are less common. The transport and deposition of atmospheric mercury depend greatly on whether the mercury is elemental or oxidized. Elemental mercury stays in the atmosphere long enough for it to be transported around the world, whereas oxidized and particulate mercury are more readily captured in existing pollution control systems or deposited relatively rapidly after their formation. As a result, most mercury in the air is in the gaseous elemental phase. Relatively little elemental mercury is deposited directly, but instead must first be oxidized.

Although gaseous oxidized mercury is very important in mercury cycling between air and other environmental compartments, the process of oxidation in the air is poorly understood, with reactions and resulting compounds yet to be verified in observations.

When mercury moves from air to water and land, it is generally in an oxidized gaseous or particulate form, whereas when it is re-emitted to air it has been converted back to gaseous elemental mercury. Sunlight appears to play a large role in both oxidation and reduction of mercury, but temperature and biological interactions are also likely to be involved to some degree. Here, too, much uncertainty remains. Nonetheless, the reactions are important in determining net deposition and fate of mercury.



Gaseous elemental mercury can be transported globally. Mercury emitted in particulate form tends to deposit closer to sources.

Monitoring of mercury in air

Monitoring of mercury in air focuses on the three primary forms of mercury. The measurement of gaseous elemental mercury is routine and robust. Measuring gaseous oxidized mercury and particulate-bound mercury, however, is challenging. Concentrations are typically very low, and these forms are chemically unstable, leading to high uncertainty in the measurements. Nonetheless, these forms are critical for defining and modelling the fate and transport of airborne mercury.

In the past two decades, coordinated mercury monitoring networks and long-term monitoring sites have been established in a number of regions, measuring mercury concentrations in the air as well as deposition of mercury in precipitation. In Europe and North America, high-quality, continuous monitoring has been going on for more than 15 years, especially in the Arctic. High-quality monitoring has started more recently in East Asia and South Africa, as part of a global effort to expand the coverage provided by long-term monitoring sites.

Measurements and trends in atmospheric mercury

Monitoring stations around the world have provided information about trends in atmospheric mercury, though the time periods vary depending on how long the site has been active. Overall, a declining trend in background mercury levels over the past decade has been recorded from monitoring stations in many regions. Other regions, however, show an increase in mercury levels.

The sites also provide information about geographical patterns, reflecting both background levels of mercury and local and regional influences. Mercury concentrations at remote sites in Asia are higher than in other regions of the Northern Hemisphere. Coastal cities in China have lower levels than inland sites, likely due to the influence of relatively clean

Trends in atmospheric measurements of mercury

Site(s)	*Period*	*Measurement*	*Trend*
Mace Head, Ireland	1996-2011	Gaseous elemental mercury	Decrease of 1.4-1.8% per year
North America, rural sites	1995-2005	Total gaseous mercury	Decrease of 2.2% to 17.4% in total
High Arctic, sub-Arctic, mid-latitudes	Up to 20 years of records	Total gaseous mercury	Decreasing trend at some stations, increasing at others

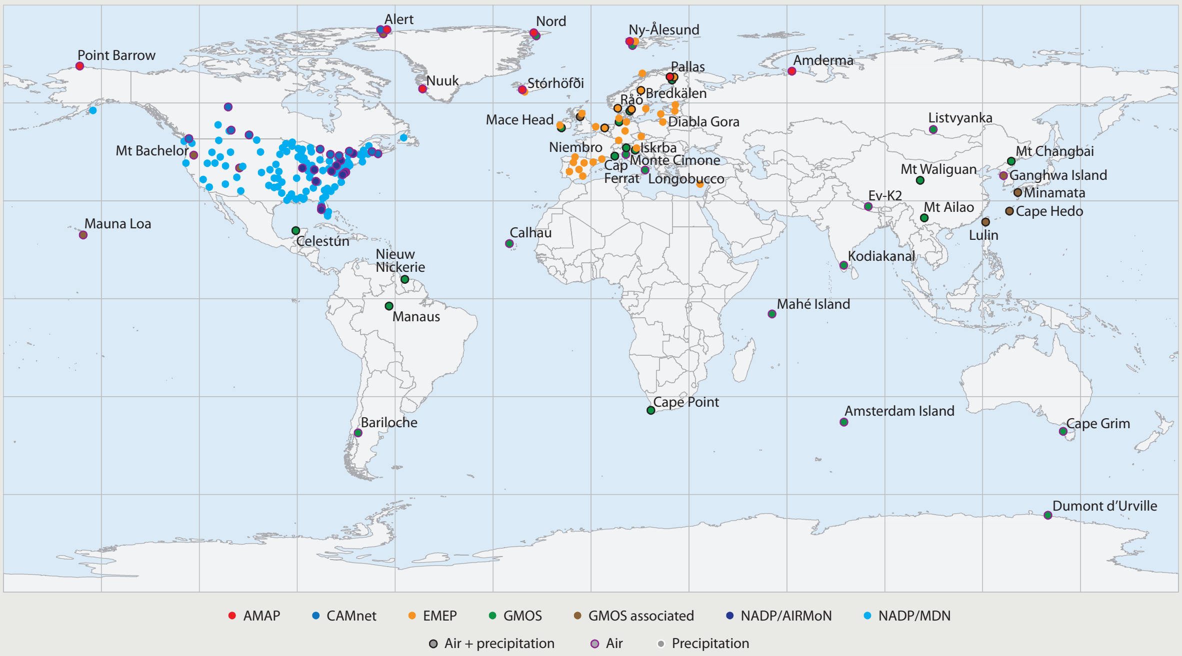
Monitoring networks

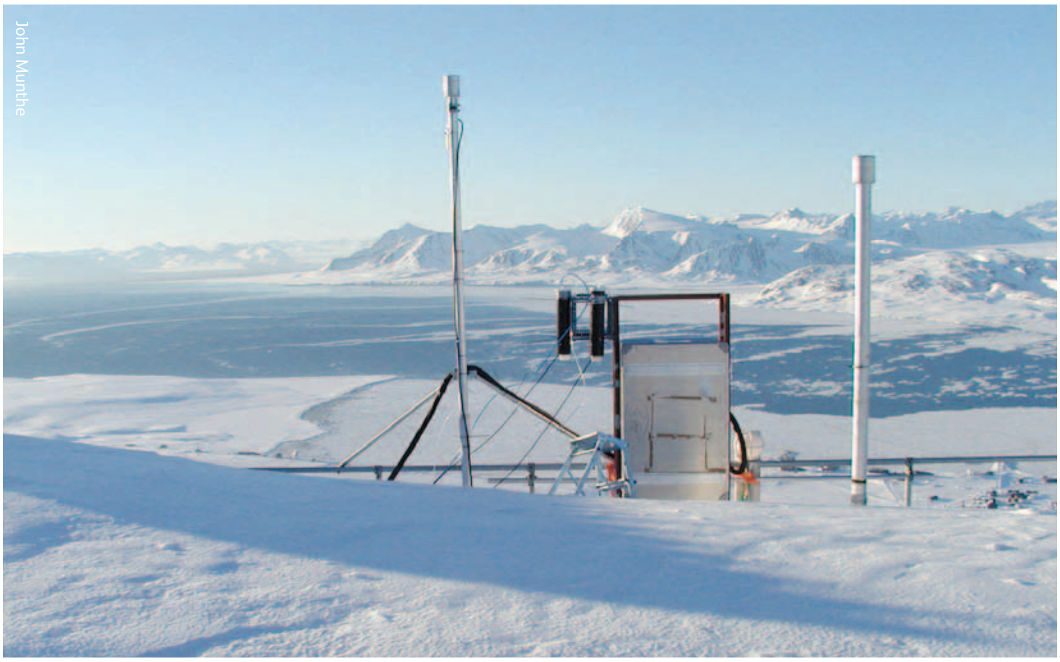
Mercury monitoring in Europe is carried out under the European Monitoring and Evaluation Programme (EMEP), one of the first international environmental measurement networks. Heavy metals such as mercury have been included in the EMEP program since 1999. Mercury measurements are available only from northern and northwestern Europe.

Three monitoring networks currently operate in North America, providing good coverage of Canada and the United States: the Mercury Deposition Network, the Canadian Air and Precipitation Monitoring Network, and the Atmospheric Mercury Network. More recently, new sites have been established in Mexico, extending coverage on the continent. The stations monitor atmospheric mercury and mercury in precipitation, which has measured since the mid-1990s. Monitoring of mercury in the air and in precipitation has been underway in Asia for nearly a decade.

The monitoring network of the Arctic Monitoring and Assessment Programme (AMAP) includes air and deposition monitoring sites located in Arctic regions of Canada, Greenland, Iceland, Norway, Russia, and Sweden.

Building on existing national and regional monitoring networks, the European Union-financed project “Global Mercury Observation System” (GMOS) started in November 2010. Its goal is to develop a coordinated global system for monitoring mercury, including a large network of ground-based monitoring stations. New sites are being installed in regions where few monitoring stations exist, especially in the Southern Hemisphere. Two sites have been established in Antarctica, one on the Antarctic Plateau and one on the coast.





The mercury background air monitoring station at Zeppelin mountain, Svalbard.

air from over the ocean. Sites off the Asian coast, however, show higher levels of gaseous elemental mercury than the Northern Hemisphere background, suggesting an outflow from the Asian mainland.

Weather patterns have also been found to have a strong influence on seasonal patterns in mercury levels in the air at monitoring sites. At the Mount Waliguan Observatory on the Tibetan Plateau, for example, northeasterly and easterly winds produced the highest levels of mercury.

Measurements at high altitudes

Measurements from ground-based stations above 2700 meters suggest that there is an inverse relationship between gaseous elemental mercury and gaseous oxidized mercury at these elevations. In other words, when there is more elemental mercury, there is less oxidized mercury, and vice versa. These measurements are in good agreement with modelling results, which gives additional confidence in current understanding of the behaviour of mercury at high altitude.

An inverse relationship between total gaseous mercury and particulate concentration has also been observed in the high stratosphere. From the transformation rate of total gaseous mercury to particulate-bound mercury, it appears that gaseous mercury lasts about two years in the stratosphere.

Atmospheric concentrations and deposition

6

Measurements and trends of mercury in precipitation

Mercury deposited by precipitation decreased from the 1990s into the 2000s at many, but not all, sites in North America and Western Europe where such measurements were taken.

Regional patterns are also evident, including slightly higher levels in southern Europe than northern Europe, and higher levels in Asia than in North America. Total mercury concentrations in precipitation in China were much higher than those in Japan and South Korea. This was mostly attributed to higher levels of gaseous oxidized mercury and particulate-bound mercury, which are readily deposited by precipitation and thus not transported far.

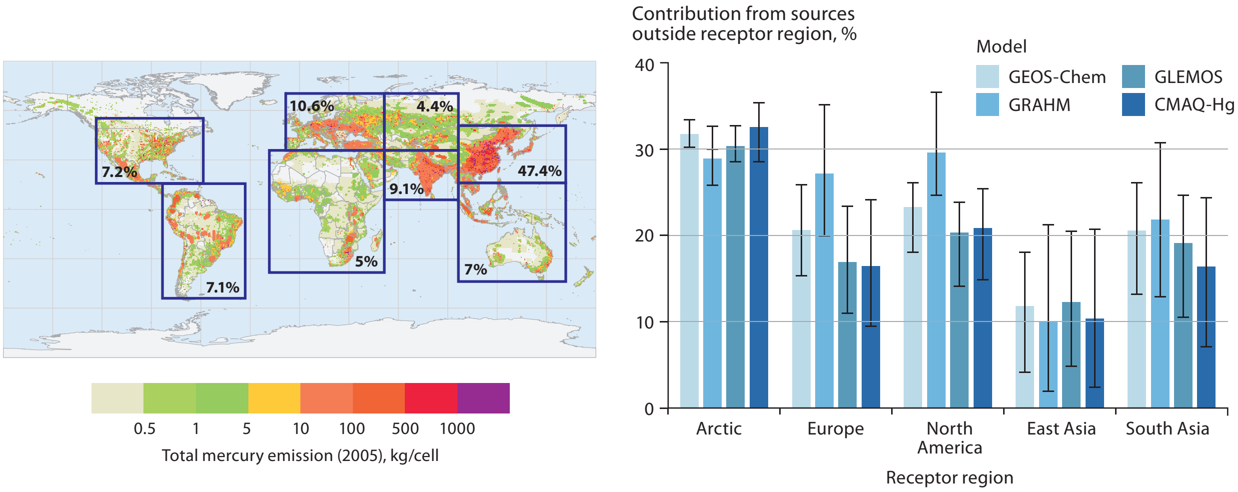
A comparison of data from Canadian and American monitoring sites found that deposition of mercury in precipitation was highest in summer.

Dry deposition of mercury, which is deposition not associated with precipitation, is difficult to measure, and consequently there is little information on trends in mercury dry deposition. This lack of information means that it is also difficult to validate model results for dry deposition.

Modelled mercury air concentrations and deposition patterns

Atmospheric mercury concentrations are highest in major industrial regions. Models examining global patterns show that East and South Asia, Europe, North America, and South Africa have the highest levels of elemental mercury in the air. Concentrations are generally lower in the Southern Hemisphere than the Northern Hemisphere because most industrial activity is in northern regions. These model results are based on simulations using the 2005 global mercury emission inventory because the 2010 inventory has only recently become available.

Intercontinental transport of mercury in the air has been examined to determine its impact on regional mercury levels. Four models using different parameters produced consistent results. Depending on the region, mercury emitted by distant sources contributes between 10% and 30% of annual mercury deposition. Where local sources are low, mercury transported from distant emission sources can account for more than half of the deposition. East Asia is the dominant source region, adding 10-14% to the deposition in



(Left) Global distribution of anthropogenic mercury emissions in 2005, with source regions that were considered in the analysis (North America, South America, Europe, Africa, Central Asia, South Asia, East Asia, Australia and Oceania) and (right) the contribution of anthropogenic sources outside a particular receptor region to deposition within the receptor region.

Modelling atmospheric transport and deposition

Global models reproduce the movement of mercury in the atmosphere, during which the mercury may move between continents. They have been effective in examining sources of mercury to the Arctic, and also for examining the outflow of pollution from South and Southeast Asia and its impact on western North America, as well as the flow from eastern North America to Europe.

Regional models, on the scale of a continent or a basin such as the Mediterranean, can provide more detail about specific source areas, even to the level of individual industrial areas. Reliable results, however, require a detailed understanding of mercury oxidation in the atmosphere, about which there is considerably uncertainty.

Most atmospheric transport models consider the full chain of mercury processes in the atmosphere. Some models also consider how mercury is cycled in other atmospheric compartments such as soil, vegetation, snow, freshwater, and seawater.

One of the largest sources of uncertainty in mercury models is the chemical mechanism used to determine how mercury changes forms in the air. Improved experimental data can help improve model performance by making sure that the correct reactions are simulated. The processes that lead from deposition to re-emission also need to be understood better. Advances in this area show promise, with model results becoming closer to estimates based on experimental data.

other regions of the world. Natural emissions and re-emissions account for 35-70% of total deposition in most regions. Deposition is generally greater in low and mid-latitudes, due to stronger sunlight, higher concentrations of oxidants, and higher precipitation.

Regional mercury models show patterns at the scales of continents or individual seas. The Mediterranean Sea, for example, is a net source of mercury, as it emits more than is deposited to it. In that region, dry deposition generally exceeds deposition of mercury in precipitation. In Central and Southern Europe, total gaseous mercury concentrations and deposition in precipitation were both consistently higher than the European average.

Across the United States, dry deposition accounts for two-thirds of total annual deposition, mainly from gaseous oxidized mercury. A study examining sources and deposition of mercury to assess the benefits of proposed emission control measures found that mercury transport from outside the country accounts for 68% of mercury deposition in the Northeast, and up to 91% in the west-central United States. Large point sources contribute up to three-quarters of nearby deposition and power plants contributed half of the deposition in the eastern part of the country. This suggests that new emissions standards would primarily benefit eastern regions of the U.S.

In Asia, studies show high seasonal variation in mercury concentration and deposition. Anthropogenic emissions are responsible for about 75% of deposition in East Asia. In this region, there is a net removal of gaseous oxidized mercury from the atmosphere, and a net export of gaseous elemental mercury.

In the Arctic, gaseous elemental mercury levels in the atmosphere are depleted rapidly in spring when, after the long Arctic winters, sunlight returns. Ozone is depleted at the same time, and it is believed that bromine-containing compounds are the cause of the photo-chemical reactions that deplete ozone and mercury. During these events, gaseous oxidized mercury and particulate-bound mercury levels increase sharply, suggesting that the gaseous mercury is oxidized and deposited, enhancing mercury deposition in Arctic areas in springtime. Recent research, however, has found that 50-80% of the deposited mercury is re-emitted within a few days. Similar springtime mercury depletion events have been seen in Antarctica.

Anthropogenic releases to the aquatic environment

7

Global assessment

Previous UNEP global mercury assessments only considered emissions to the atmosphere. The 2013 Report presents the first attempt at compiling a global inventory of mercury releases to aquatic environments. Releases directly into the aquatic environment present a completely different chemistry, set of pathways, and fate to those released to air. They are also more directly linked to the risks posed by mercury to global environmental and human health. Unlike mercury releases to air, which are predominantly in the form of gaseous elemental mercury, releases to water are predominantly inorganic mercury and to a lesser extent liquid elemental mercury.

At present, only some sources of aquatic releases can be quantified with any confidence. Thus, many sources that may be important are not included in this first assessment of global aquatic releases. For example, land management practices that expose new geological sources of mercury in rocks and mineral soils, or that re-mobilize previously deposited mercury, cannot yet be assessed. Two broad categories of current anthropogenic sources are considered here: point sources of mercury release to water, and diffuse releases of mercury as a result of its remobilisation from areas where it was previously deposited or accumulated due to human activity (i.e., contaminated sites). Artisanal and small-scale gold mining (ASGM), mercury-containing pesticides and fungicides used in agriculture, and deforestation are considered separately.

The global estimate of mercury release to water from **point sources** has been derived from the atmospheric emissions assessment and the approach employed in the UNEP Toolkit to partition total mercury releases between air, land, and water. This approach has considerable uncertainty and may omit sectors where releases to water are high but air emissions are unimportant and therefore not addressed in the inventory. Global releases from point sources were estimated to be 185 tonnes per year.

For **diffuse sources**, evaluating the relative contribution of anthropogenic and natural sources to the aquatic environment requires determining considerations of the various mercury inputs. For some sectors, data exist that allow a preliminary assessment of the amounts of mercury re-mobilized into aquatic systems.

For **mercury-contaminated sites**, the range of average soil concentrations of mercury reported for sites where mercury was mined, used, or otherwise released by human activity was considered. The area of contamination is then used to determine how much mercury is available in soils and, when combined with a factor for how much mercury is released from those soils in a year, the total release can be estimated. Among identified contaminated sites, mercury mining is identified as the largest sector, followed by mining of precious metals. Total releases to aquatic environments from contaminated sites are estimated to be 8.3-33.5 tonnes per year.

Point source releases to water from various sectors, in tonnes per year with the range of the estimate, and as a percentage of total anthropogenic emissions.

Sector	Releases (range), tonnes
Non-ferrous metal production	92.5 (19.3 - 268)
Consumer product waste	89.4 (22.2 - 308)
Chlor-alkali production	2.8 (1.0 – 5.5)
Oil refining	0.6 (0.3 – 1)
Grand Total	**185 (42.6 – 582)**

Releases to water from contaminated sites, in tonnes per year with the range of the estimate.

Sector	Releases (range), tonnes
Primary mercury mining sites	6.7 – 26.6
Precious metal production sites	1.4 – 5.5
Non-ferrous metal production sites	0.1 – 0.5
Chlor-alkali production sites	0.1 – 0.5
Other industrial sites	0.1 – 0.3
Grand Total	**8.3 – 33.5**

Much of the mercury released from **artisanal and small-scale gold mining** goes into rivers, lakes, soils and sediments, and tailings. From soils and tailings, it may be re-mobilized by leaching and erosion. In addition, mining may disturb mercury-containing soils and sediments that may then erode more quickly, releasing more mercury than would otherwise have become available from natural erosion. A key factor in these processes is the local hydrological cycle of precipitation, evaporation, run-off, and river flow. To account for this in the assessment, countries were designated as dry, wet, or intermediate, to determine the relative importance of erosion. The tropical and subtropical countries which have the greatest activity in this sector also tend to experience high precipitation and run-off, exacerbating this source of mercury release and re-mobilization. Total worldwide releases of mercury to land and water from ASGM were estimated at over 800 tonnes per year. How much of this is released to water cannot yet be determined.

Mercury continues to be used in **pesticides and fungicides**. 2100 tonnes of mercury were released in the decade of the 1960s through such agrochemical uses. Current data are unavailable, although the use of mercury in these products has been greatly reduced.

Deforestation, especially in the Amazon Basin, can lead to extensive soil erosion and thus the release of mercury previously accumulated in soils. Using 2010 figures for deforestation rates around the world, and an estimate of soil concentrations of mercury, as much as 260 tonnes of mercury may have been released into rivers in 2010 as a result of deforestation worldwide.

Because this is the first attempt to quantify global mercury releases to the aquatic environment, there is no previous measurement against which these results can be compared. Thus, it is not possible at this time to evaluate trends in releases.

Uncertainties in release estimates

Estimating global releases of mercury to aquatic environments is being done here for the first time. Many data are missing, and others are imprecise. A number of assumptions have been made, based on what measurements are available or on other grounds, to extrapolate from known quantities or to calculate aquatic releases in relation to atmospheric or other emissions. Thus, the results should be treated with great caution. It is nonetheless clear that anthropogenic sources and human activity contribute hundreds of tonnes of mercury to aquatic environments each year, a substantial amount relative to estimated natural releases 150-960 tonnes per year from terrestrial environments.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Bureau of Land Management

Contaminated sites (top), erosion following deforestation (middle) and a flooded store of mercury-contaminated waste (lower) illustrate potential sources of mercury releases to water.

Aquatic pathways, transport, and fate

8

Mercury in aquatic environments

The pathways and fate of mercury in aquatic environments are important because it is in waters, sediments, and wetland soils that inorganic mercury is converted into methylmercury, which is toxic and concentrates in animals. The majority of human exposure to mercury, and the health risk that comes with mercury exposure, is from consumption of marine foods. Thus, this section focuses on the world's oceans. Some freshwater systems, however, are important sources of fish for human consumption, especially for subsistence and recreational fisheries, often among indigenous peoples. Artisanal and small-scale gold mining (ASGM) communities may also be affected through fish consumption and drinking water, if those are contaminated by local releases.

The major processes of mercury cycling are generally similar for all aquatic systems. Inorganic mercury in dissolved or particulate form is the dominant mercury type in most marine and fresh waters. Dissolved gaseous elemental mercury accounts for less than 30% of total mercury in water. Methylmercury is often present at trace levels, but may in some settings reach 30% of total mercury. In freshwater and coastal environments, inorganic mercury is transformed into methylmercury primarily in sediments. In the open ocean, this conversion takes place largely at intermediate depths, between 200 and 1000 meters in the water column. Mercury is lost from aquatic systems in two ways. When inorganic mercury is reduced to elemental mercury, it can be re-emitted to the atmosphere. When inorganic mercury binds to particulates in water, it can settle out rapidly and be buried in sediments. Deep burial in ocean sediments is one of the major pathways by which mercury is removed from the biologically active environment.

The global mercury cycle is chemically and physically complex. Thus, it is necessary to use models to study, describe, and predict what happens and will happen to mercury in the aquatic environment. Until recently, only one model existed that incorporated air, land, and water into a unified whole. The model has been validated against observations of mercury, and represents the current scientific consensus. The largest potential errors in this model in terms of the aquatic cycle concern details of the exchange of mercury between air and water.

Pathways and fate of mercury in the oceans

Model simulations suggest that anthropogenic impacts on mercury levels in the ocean are greatest in the surface waters, the top 100 meters or so of the water column. While model results vary, one recent estimate suggests that anthropogenic emissions over the last 100 years have doubled the concentration of mercury in the surface layer of the ocean, and increased it by 25% in intermediate waters, and by 10% in deep waters. The difference is due to the length of time it takes for surface waters to circulate to the depths.

Models and measurements agree that direct deposition from the atmosphere is the dominant pathway by which mercury reaches the oceans. The exceptions are smaller, semi-enclosed basins such as the Mediterranean Sea or the Arctic Ocean, where river runoff, coastal erosion, and ocean currents


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account for about half of mercury inputs. The most recent modelling effort suggests that total deposition input of mercury to the oceans in 2008 was 3700 tonnes.

Other mercury pathways appear less important on a global basis. Rivers are estimated to carry more than 2800 tonnes of mercury each year, but only about 380 tonnes of this is transported offshore. The rest is trapped by particles in estuaries. Groundwater and re-mobilization from sediments provide 100-800 tonnes of mercury to the oceans each year. Undersea hydrothermal vents add less than 600 tonnes of mercury to the oceans. There are high concentrations of mercury in vent fluids, but a great deal of the mercury is precipitated as solids once the vent fluids enter seawater.

Models suggest that, globally, about 70% of the mercury deposited into the ocean is re-emitted to the atmosphere. Oxidized mercury in surface waters is reduced by biological and photochemical processes to the elemental form that is volatile and readily re-emitted. The removal of this mercury ultimately reduces the pool of mercury that could be converted to methylmercury and be accumulated by marine organisms. The re-emission process thus simultaneously prolongs the lifetime of mercury cycling through the atmosphere and upper ocean, and acts to reduce mercury availability for marine food webs.

Any changes in the efficiency of mercury reduction in surface waters or the rate of re-emission is likely to impact mercury concentrations in surface waters and the air. One example is the effect of sea ice in the Arctic Ocean, which blocks the re-emission of elemental mercury, leaving elevated levels in waters under ice. Changes in primary productivity could change the rate at which mercury is bound to particles, thus affecting re-emission to the atmosphere as well as rates of downward transport in the ocean. Changes in oxidant levels in the atmosphere, such as ozone and bromine, may also influence the rate of oxidation of gaseous elemental mercury and thus deposition rates to the ocean.


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Mercury accumulated in marine food-webs can enter the human diet.

Methylmercury in the ocean

Natural bacterial processes in seawater, and in sediments in coastal environments, convert inorganic mercury to methylmercury. Methylmercury levels are highest in the subsurface waters of many oceans because it is formed at these intermediate depths, likely as a result of the decomposition of organic material falling from surface waters. Current understanding indicates that about 300 tonnes of methylmercury is produced in the upper ocean by this and related processes. By contrast, only about 80 tonnes of methylmercury reaches the ocean from other sources such as atmospheric deposition, rivers, and diffusion from sediments.

Current modelling indicates that methylmercury stays in the upper ocean for about 11 years. De-methylation, by photochemical reaction or by microbial activity, is the major removal process for methylmercury in the ocean. About 240 tonnes of methylmercury is removed by this process from the surface waters of the ocean per year.

The other important pathway for methylmercury in seawater is uptake into marine food webs. Although only about 40 tonnes per year is taken up in this way, it is this fraction that poses risks to marine animals and human consumers of seafood. Methylmercury is a problem for several reasons. First, it is taken up by plankton much more efficiently than is inorganic mercury, resulting in concentrations in plankton that are as high as 10,000 times the concentration in seawater. Second, methylmercury is absorbed through the intestine of animals much more easily than is inorganic mercury. Third, methylmercury biomagnifies as it moves up the food web. Thus, methylmercury becomes an increasingly greater proportion of the mercury in organisms higher in the food web. This explains why some indigenous populations that consume top marine predators such as fish, seals, and whales have some of the world's highest concentrations of methylmercury, giving rise to health concerns.

Pathways and fate of mercury in freshwater

Observations and modelling both show that there are in general many similarities between mercury chemistry, pathways, and fate in lakes and in the oceans, but with obvious differences in scale and in the relative importance of different processes. Modelling of mercury dynamics was done for four lakes with a history of direct mercury inputs, from the largest freshwater lake in the world (Lake Superior) to small lakes in Ontario, Canada. Atmospheric deposition and river inflow were the main sources of inorganic mercury. Much of the mercury input from lake and river catchments was associated with dissolved and particulate organic matter. The dominant mercury removal mechanisms, as in saltwater, were burial in sediments and photochemical reduction of oxidized mercury to elemental mercury followed by re-emission to the air. In Lake Superior and Lake Michigan, there is evidence for methylation of mercury in the water column, as is seen in the open ocean.

Methylmercury levels in freshwater fish vary with the level of deposition of mercury from the air, though other factors such as inputs from the watershed and the number of trophic levels within the lake's food web are also important. Methylation predominantly occurred in lake sediments and wetlands and floodplain soils, where sulphate-reducing bacteria are believed to be primarily responsible. Methylmercury is de-methylated in sediments and also taken away in the outlet river from each lake.

Some 400-1400 tonnes of mercury are estimated globally to be trapped behind dams and other man-made impoundments each year. This has in many cases led to significant increases in total mercury and methylmercury levels in water, and of methylmercury in fish and other aquatic species. When artificial lakes are created, plant material is submerged, leading to decay and anoxia. In these conditions, microbially driven methylation of inorganic mercury takes place. In some cases, the elevated mercury levels have also been observed downstream from the artificial lakes and reservoirs.

Anthropogenic impacts on aquatic mercury levels

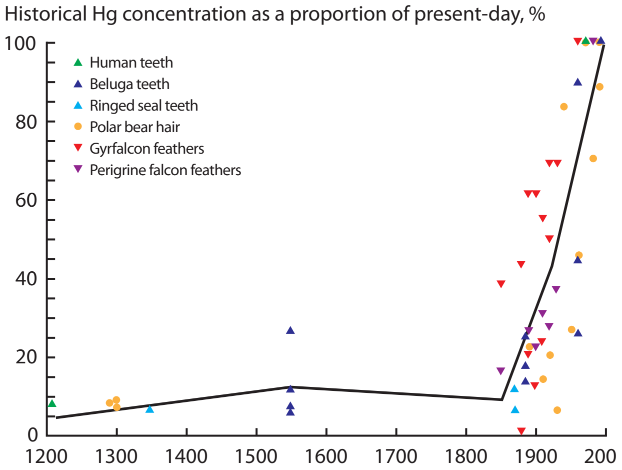
Two studies have reported that the Atlantic and Pacific Oceans have shown opposing trends over recent decades. While the influence of changing ocean currents and other oceanographic factors may be a factor, the trends do make sense in light of patterns of anthropogenic emissions. In the North Pacific Ocean, mercury concentrations appear to have increased at depths between 200 and 1000 meters over the last few decades. This increase coincides with the rapid industrialization of East Asia.

In the North Atlantic, however, results from near Bermuda suggest a substantial decrease in mercury concentration and a change in the mercury profile through the water column. The Mediterranean Sea, too, showed a decrease in mercury concentration between 1990 and 2004. These findings are consistent with atmospheric data from around the North Atlantic. The conclusion is that mercury levels in seawater in the North Atlantic were elevated by human activity but may now be declining, likely as a result of decreased emissions from North America and Europe.

A complementary approach to measuring mercury in seawater is to measure mercury in aquatic animals, which accumulate and integrate mercury over time. Teeth, hair, feathers, and eggshells are useful long-term archives of mercury concentrations, and can provide data from the pre-industrial period (i.e., before 1800) as well as more recent periods.

Among marine animals, samples are available from several regions, particularly from the Arctic, where cold, dry conditions help preserve animal tissues. Mercury concentrations between the 13th and 16th centuries were relatively stable. From the mid- to late 19th century to the end of the 20th century, mercury levels increased by an average of 12 times. On average, therefore, about 92% of the mercury in Arctic marine wildlife today is likely to be of anthropogenic origin.

Similar findings were found for a 700-year sequence of seabird eggshells from the South China Sea. Mercury levels increased steadily between 1800 and 2000, with a particularly rapid increase after 1970. Concentrations since 2000 are about 10 times higher than pre-industrial levels, with 91% of the mercury now likely to be of anthropogenic origin. In the Antarctic, studies of seal hairs show that pre-industrial mercury levels were only 60% of recent levels. The relatively small difference



Analysis of museum samples reflects the increase in mercury emissions and releases since the mid-19th century associated with anthropogenic activities.

between pre-industrial and modern mercury levels in Antarctic is consistent with lower mercury emissions and atmospheric concentrations in the Southern Hemisphere as compared with the Northern Hemisphere.

The timing of long-term increases of mercury in aquatic animals can shed light on the likely sources of mercury emissions that were responsible. The industrialization of Europe and North America appear responsible for the large increases in marine mercury levels that began in the 19th century, as these increases occurred prior to recent Asian industrialization. As with water concentrations in the Pacific Ocean, recent rapid increases in mercury in seabird eggs in the South China Sea coincide with industrialization in Asia.

The time lag in aquatic ecosystem response

One important conclusion from air-ocean modeling is that the oceans have not yet reached equilibrium with current atmospheric levels of mercury. This lag is due to several factors. First, mercury stays in the upper ocean, above 200 meters depth, for about 30 years, and for centuries in intermediate and deep waters. This is much longer than the one year residence time in the lower atmosphere. Thus, removal from the ocean takes much longer than does removal from the air, and so concentrations will change more slowly.

Second, because of the long lifetime of mercury in deeper ocean waters, a great deal of natural mercury is present in the ocean already, about 100,000 tonnes out of a total of 135,000 tonnes in intermediate waters, and 200,000 out of 220,000 tonnes in deep waters.

Third, vertical transport of mercury from intermediate depths back to the surface returns a substantial amount of mercury to the biologically active zone each year. As a result, average mercury concentrations in seawater and marine animals are likely to increase slowly for decades if not centuries, even if atmospheric levels stabilize at present levels. In short, the effects of historical anthropogenic emissions from Europe and North America are still being observed in the oceans, at the same time that the effects of the recent rise in emissions from Asia are being seen.

Regionally, different trends can be expected depending on distance from sources and ocean circulation patterns. In the North Atlantic, north of 55° N, it will take 50-600 years to achieve equilibrium between atmospheric and seawater mercury levels. In the North Pacific, this process is estimated to take 500-700 years, and in the Antarctic, 700-1000 years. The Arctic Ocean, by contrast, is smaller and will only take about 35 years to reflect changes in atmospheric mercury levels. Surface waters of the Mediterranean Sea should show also changes within 10-50 years.

Time lags in the responses of many freshwaters and their food-webs to changes in atmospheric mercury levels are also expected. Although some immediate recovery following reductions in atmospheric mercury deposition rates is likely, full recovery may take decades, centuries, or longer depending on the characteristics of the area. Highly polluted freshwaters with catchments and sediments containing large amounts of anthropogenic mercury will recover most slowly, as is already observed around point sources such as smelters that have closed down.

9

Major gaps in knowledge

Large uncertainties remain in global estimates of mercury emissions to the air. These stem from various sources, including the availability of information on activity levels, but mainly from the lack of information concerning the mercury content of some raw materials and the validity of assumptions regarding processes and technologies employed to reduce mercury emissions, including their rates of application and effectiveness. The accuracy and precision of measurement-based estimates can depend on the validity of extrapolating measurements made at infrequent intervals to longer periods, or measurements made at one plant to other facilities with similar operations.

Potentially important emissions sectors that are still not quantified in the emissions inventory include the use of mercury in vinyl-chloride monomer production; secondary metals production; oil and gas extraction, transport, and processing; industrial and hazardous waste incineration and disposal; sewage sludge incineration; and dental fillings preparation and removal.

Current measurements and their evaluation are inadequate for determining spatial and temporal trends. Improved, more extensive, and better coordinated measurements are needed. A permanent global integrated monitoring network for atmospheric mercury and mercury deposition is needed to achieve this goal. The atmospheric network sites should be closely integrated with water, soil, and biological monitoring networks. The results can be used for model testing and evaluation as well as for more accurately detailing the geographic impact of anthropogenic emissions. Monitoring of mercury concentrations in the important marine food species is essential to understanding possible human health impacts and the effects of future emissions changes.

Better data on mercury distribution in the troposphere is needed to improve understanding of long-range transport and source-receptor relationships. Coordinated studies at high altitudes and by aircraft are needed. This information will also help validate regional and global scale models, improving their prediction capabilities with regard to different policy scenarios.

Key processes related to global transport and cycling of mercury remain inadequately understood. The chemical form of gaseous oxidized mercury is unknown. Reduction and oxidation rates for mercury in the presence of atmospheric oxidants need further study, including determining which oxidants are important. New measurements and modelling studies are needed to examine key chemical and physical processes that affect global transport and cycling.

Few data are available for reporting mercury releases to aquatic systems. Systematic and consistent monitoring of mercury releases to the air is required, especially for contaminated systems. Releases of mercury from soils into waters depend greatly on climate and topography, and these parameters need to be better accounted for. Consistent approaches for measuring and reporting releases from point sources are needed to ensure comparability of data from around the world. In particular, the actual role of artisanal and small-scale gold mining (ASGM) in emissions to air and releases to water needs to be more accurately estimated.

The link between mercury deposition, methylation, and uptake by living organisms needs further study. The parameters that determine the rates of exchange of mercury compounds between air and sea, air and soil, and air and vegetation are not fully understood. Whole-ecosystem studies of mercury are needed to better understand biogeochemical cycling. Methylation/demethylation rates, and their spatial and temporal variations and relationship to climatic factors, need to be determined in most of world’s major ocean basins, as well as in representative freshwaters.

10

Key findings of the 2013 assessment

Atmosphere

Total anthropogenic emissions of mercury to the atmosphere in 2010 are estimated at 1960 (1010-4070) tonnes which is about 30% of the total mercury that was emitted and re-emitted from anthropogenic and natural sources in that year. The largest anthropogenic sources are associated with artisanal and small-scale gold mining (ASGM) and coal burning, which together account for about 62% of the annual total anthropogenic emissions to air. Other major sectors include ferrous and non-ferrous metal production and cement production.

East and Southeast Asia are responsible for about 40% of global anthropogenic emissions. About 75% of the mercury from this region comes from China, which is about one-third of the global total. Increased estimates for emissions from ASGM, largely a result of newly obtained data and improved information, mean that South America and Sub-Saharan Africa are also responsible for a greater proportion of global emissions than was previously assumed.

Anthropogenic emissions over time have increased mercury loads present in the environment. This leads to higher rates of re-emission, and also means that there will be a time lag of years or decades between emissions reductions and lower mercury levels in the food web, including pathways of human exposure.

Mercury emissions to the atmosphere likely peaked in the 1950s to 1970s and subsequently declined because of reductions in Europe, Russia, and North America. Emission trends are unclear due to changes in methods employed to produce inventories and differences in the sectors that have been accounted at different times. There are, however, some indications that emissions may be rising again, with increases from East Asia offsetting continuing reductions in Europe and North America.

Aquatic environments

Natural processes in aquatic systems convert less toxic elemental and inorganic mercury into much more toxic methylmercury. Methylmercury concentrates and accumulates in the food web, leading to high concentrations in some species of seafood and fish that many people eat.

Anthropogenic releases of mercury to aquatic environments contribute hundreds of tonnes to the amount of mercury cycling in the environment. Diffuse releases and point sources appear equally important. Atmospheric deposition, however, remains the most important input of mercury to land and oceans, and has increased the amount of mercury in many environmental compartments by a factor of two or three since the start of the industrial age. On land, mercury that is deposited is largely retained in soils and vegetation, increasing the available pool for re-mobilisation to adjacent aquatic systems. Re-emission from soils, however, is a major addition to atmospheric mercury.

Hydrology is the most important factor in the transport of mercury from catchments to downstream environments. Relatively little of this mercury reaches the open ocean, as most is captured in sediments behind dams, in estuaries, and near the coast. Changes in land cover and land use can have a large effect on mercury mobilisation, as exposed soils erode and mercury leaches into the water table.

Concentrations of mercury in Arctic marine animals today are about 10-12 times higher than in pre-industrial times (i.e., prior to about 1800). This means that on average about 92% of the mercury in marine predators such as seabirds, seals, and whales is anthropogenic in origin. The timing of the increase suggest that 19th and early 20th century emissions from Europe, North America, and Russia were responsible. Increases mercury concentrations in seabirds in the South China Sea appear to be more recent than the Arctic increases, coinciding with increasing industrialisation in East and Southeast Asia.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Recovered mercury is being stockpiled at long-term storage sites above- and, as shown here, below ground.

The upper 100 meters of the oceans have twice the mercury that they did a century ago. Intermediate and deeper waters have 10-25% more mercury on average, reflecting the slow transport of mercury downwards in the oceans. Seawater concentrations will thus be especially slow in responding to changes in mercury inputs from atmospheric deposition and river flow. As a result, mercury concentrations in marine biota are likely to increase slowly for decades to centuries, even without an increase in atmospheric emissions.

In freshwater ecosystems, atmospheric deposition and re-mobilisation from soils slow the reduction of mercury levels, even in regions where atmospheric concentrations have decreased due to emission controls.

Further increases in atmospheric emissions will have long-term consequences for commercial fisheries and all consumers of marine and freshwater foods.

It is likely to be years or decades before reductions in anthropogenic emissions and releases of mercury have a demonstrable effect on mercury levels throughout the environment and in the fish and marine mammals which are part of the human food-chain. This only reinforces the need to act now to continue and strengthen international efforts to reduce current mercury emissions and releases. Delays in action now will inevitably lead to slower recovery of the world's ecosystems in future from mercury contamination, leaving an even greater legacy of pollution for future generations.

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AMAP

Global Mercury Modelling: Update of Modelling Results in the Global Mercury Assessment 2013

MSC-E

МСЦ-В

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Contents

Acronyms

AMDE	Atmospheric Mercury Depletion Event
ASGM	Artisanal and small-scale gold mining
CIS countries	Countries of the Commonwealth of Independent States
FAO	UN Food and Agriculture Organization
GEM	Gaseous elemental mercury
GEOS-Chem	Chemical transport model, Massachusetts Institute of Technology
GLEMOS	Chemical transport model, Meteorological Synthesizing Centre - East
GMA 2013	Global Mercury Assessment 2013
GMHG	Chemical transport model, Environment Canada
GOM	Gaseous oxidized mercury
PBM	Particle bound mercury

1. Introduction

The Global Mercury Assessment 2013 (GMA 2013) (AMAP/UNEP, 2013) was prepared in accordance with the request of the UNEP's Governing Council (Decision 25/5 III, paragraph 36) to support negotiations on the development of the Minamata Convention on Mercury, a global treaty to reduce mercury pollution adopted by governments in October 2013. GMA 2013 covered a variety of aspects of the fate and transport of mercury in the environment including emissions to air and releases to the aquatic environment, dispersion and chemical transformations in the atmosphere and aquatic environment, and exchange fluxes between different environmental media. The assessment paid particular attention to the development of an up-to-date global inventory of anthropogenic mercury emissions. Evaluation of mercury pollution on a global scale was based on the analysis of available observational data and modelling results.

The current report aims to update the information presented in section 3.6 of the Technical Background Report for the Global Mercury Assessment 2013 (AMAP/UNEP, 2013) with new model simulation results and focusing on an evaluation of mercury intercontinental transport and source attribution of mercury deposition. The character of mercury dispersion in the atmosphere and transport from one region to another is largely affected by the physicochemical properties of the atmospheric mercury species. Poorly soluble and relatively stable gaseous elemental mercury (GEM) can drift in the air for months providing transport of mercury mass between different regions of the planet. In contrast, oxidized mercury species – gaseous oxidized mercury (GOM) and particle bound mercury (PBM) – are easily removed from the air by precipitation scavenging or surface uptake (Selin, 2009; Travnikov, 2011; AMAP/UNEP, 2013). Therefore, levels of mercury deposition and its source apportionment in each region are determined by the magnitude and speciation of domestic emissions, emissions in other regions and by the oxidative capacity of the atmosphere that transforms globally dispersed GEM to deposited GOM and PBM. As has been shown in previous studies (Seigneur et al., 2004; Selin et al., 2008; Travnikov and Ilyin, 2009; Corbitt et al., 2011; Lei et al., 2013; Chen et al., 2014), atmospheric transport from distant sources can make a significant contribution to mercury deposition, particularly in regions with low domestic emissions. On the other hand, the proportion of anthropogenic emissions that deposit locally or regionally depends on emissions speciation, which differs significantly for different emission sectors. Besides, the impact of long-range transport on mercury deposition can vary seasonally due to change in air concentrations of mercury oxidizing agents that lead to change in GEM oxidation intensity and subsequent deposition.

The current study is based on multi-model simulations of mercury atmospheric transport performed as part of the Mercury Modelling Task Force (MMTF), a scientific cooperative initiative under the Global Mercury Observation System (GMOS, www.gmos.eu), aimed at improving current understanding of the key mercury atmospheric processes and evaluating present and future levels of mercury pollution. Simulation results of the multi-model ensemble (see Annex A) are used to quantify global patterns of mercury air concentration and deposition (Chapter 2), source apportionment of mercury deposition to major geographical regions and aquatic areas of the global ocean as well as seasonal variation in source-receptor relationships (Chapter 3), and deposition from different emission sectors (Chapter 4). Simulation results for each individual model of the ensemble are presented in Annex B.

2. Global patterns of mercury air concentration and deposition

An ensemble of three chemical transport models (GLEMOS, GEOS-Chem, GMHG) was applied for evaluating atmospheric mercury dispersion and deposition on a global scale in 2013. A brief summary of the main features of the participating models is given in Annex A. The models also took part in the multi-model assessment of mercury pollution presented in GMA 2013 (AMAP/UNEP, 2013). The models differ significantly in their formulation including different horizontal and vertical resolution, and differences in their description of mercury atmospheric chemistry and their parameterization of specific processes (e.g. dry and wet deposition, atmospheric mercury depletion events – AMDEs – in the polar regions etc.). Two of the three models (GLEMOS and GMHG) are mainly atmospheric models simulating mercury transport in the atmosphere and exchange with the Earth's surface (deposition and re-emission), whereas the remaining model (GEOS-Chem) presents a full multi-media description of mercury cycling in the environment. The models also differ in their estimates of natural and legacy emissions of mercury to the atmosphere. Thus, the multi-model ensemble reflects the range of contemporary approaches applied for simulations of mercury contamination and partly characterizes uncertainties associated with gaps in knowledge on mercury processes in the environment.

The global inventory of mercury anthropogenic emissions for 2010 (AMAP/UNEP, 2013) was used in the present study. The dataset consists of gridded emission data with a spatial resolution of 0.5° × 0.5° for three mercury species (GEM, GOM, PBM). The total global emission of mercury from anthropogenic sources is estimated at 1875 t/y. This estimate of total emissions is somewhat lower than the total mercury emission reported in GMA 2013 (1960 t/y), because it does not include emissions from contaminated sites which were not spatially distributed (AMAP, 2014). The overall proportions of GEM, GOM, and PBM emissions are 81%, 15% and 4%, respectively. This is based on a simple emissions speciation scheme applied to the primary sector emissions estimates, which also assigned emissions to three classes of source height: h ≤50 m, h = 50–150 m, h ≥ 150 m. It should be noted, however, that some models of the ensemble modified the original anthropogenic emissions speciation scheme mentioned above following the model formulation (Annex A, Table A-1). There is no information on temporal variation of emissions available in the dataset.

The spatial distribution of the total annual anthropogenic mercury emission over the globe in 2010 is illustrated in Figure 1a and the speciation of emissions in different geographical regions in Figure 1b (see Chapter 3 for a definition of the source regions). Significant mercury emissions are characteristic of industrial regions in East and South Asia, Central Europe and the eastern part of North America. These regions are also characterized by an increased share of oxidized mercury forms (GOM and PBM). In addition, high emission fluxes are typical for some areas of Central and South America, Sub-Saharan Africa and Southeast Asia due to mercury releases from artisanal and small-scale gold mining (ASGM), mostly as GEM. Almost no emissions are expected in the Arctic and Antarctic regions.

The simulated spatial distribution of GEM in ambient air and total mercury deposition fluxes are shown in Figure 2. The concentration of GEM has a pronounced south-to-north gradient (Figure 2a). Mercury concentrations in the southern hemisphere are mostly below 1.2 ng/m³, whereas concentrations in the northern hemisphere range between 1.3 and 1.4 ng/m³ over the ocean and commonly exceed 1.4 ng/m³ over land. GEM concentrations in East and South Asia are higher than those in Europe, which in turn are somewhat greater than those in North America. This pattern generally reflects the spatial distribution of anthropogenic mercury emissions (Figure 1a). Elevated concentrations simulated by the models in the northern part of South America and in Sub-Saharan Africa are caused by a large contribution of emissions from ASGM. .

The calculated global distribution of mercury deposition in 2013 is shown in Figure 2b. Along with high mercury deposition fluxes over large industrial regions (East and South Asia, Europe, North America etc.) and regions with significant mercury emissions from ASGM (Southeast Asia, Central and South America, Sub-Saharan Africa) relatively large deposition

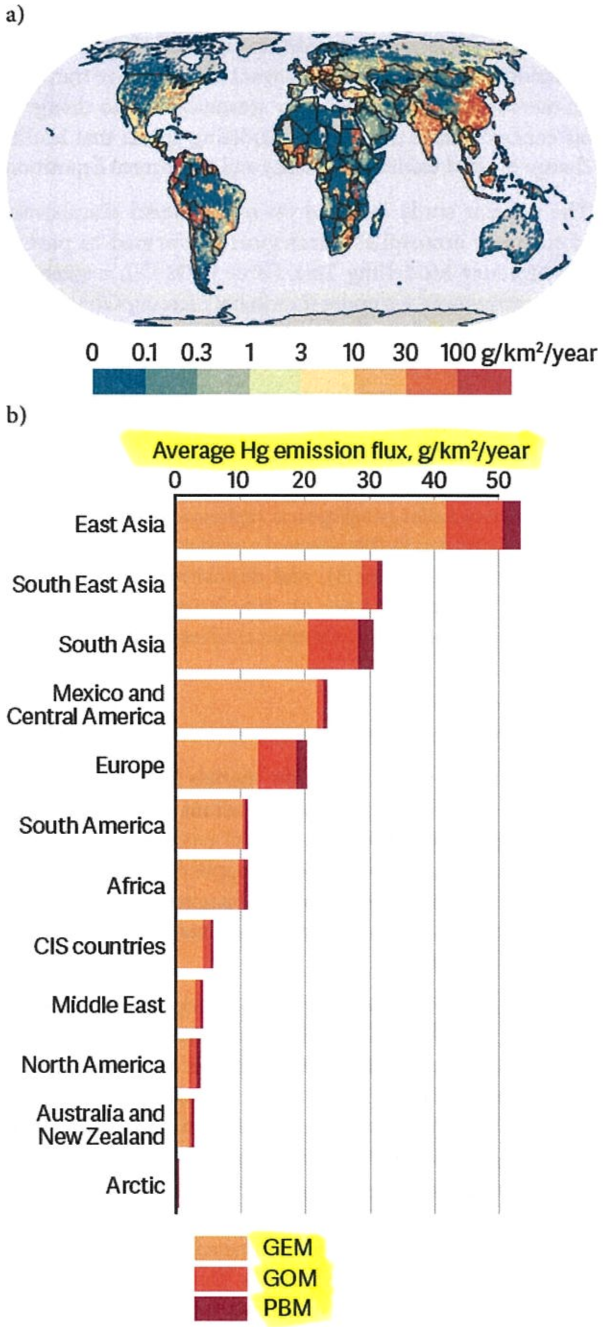


Figure 1. Global distribution of anthropogenic mercury emissions in 2010 (a) and speciation of mercury emissions for in different geographical regions (b)

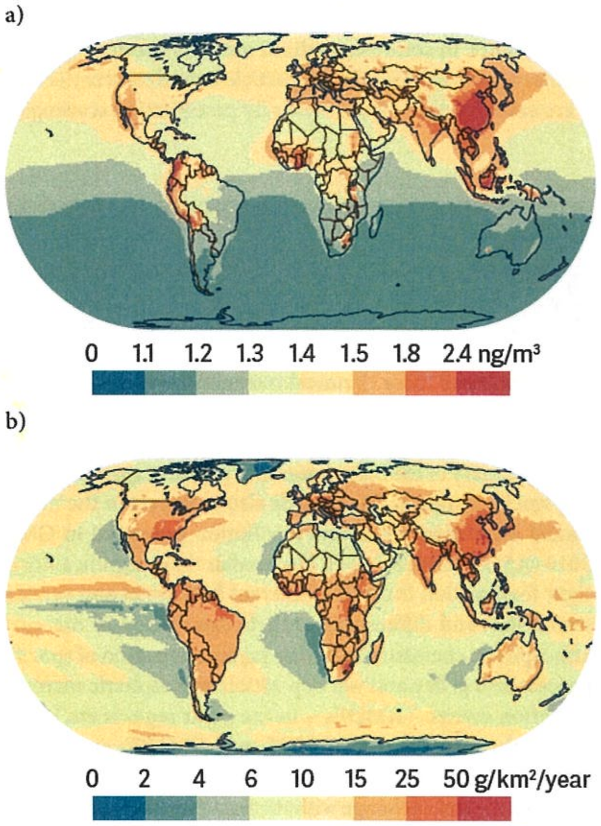


Figure 2. Global distribution of ensemble mean annual GEM concentration in ambient air (a) and annual total mercury deposition (b) in 2013.

is also detected over some remote areas of the oceans and in the polar regions. The former includes, for instance, elevated mercury deposition in the Intertropical Convergence Zone (ITCZ; a belt of converging trade winds and rising air that encircles the Earth near the equator) due to high precipitation intensity. The latter is characterized by intensive oxidation of GEM in the lower troposphere during AMDEs, leading to increased mercury deposition in spring.

Atmospheric deposition of mercury includes a significant contribution from natural and legacy sources. The relative contributions of contemporary anthropogenic emissions and natural/legacy emissions are shown in Figure 3. The graphic also includes average mercury deposition fluxes in various geographical regions. The relative contributions of the two source types are comparable in size only in three source regions – South Asia, East Asia and Europe. In the other regions the share of current anthropogenic sources varies between 20% and 35%. The contribution of natural/legacy sources is generally greater in remote regions with lower atmospheric deposition. It should be noted that the three models agree relatively well in their simulation of current anthropogenic deposition (see Annex B, Figure B-3). In contrast, estimates of mercury deposition from natural/legacy sources vary within a factor of 2 indicating higher uncertainty of the multi-model results for this deposition component.

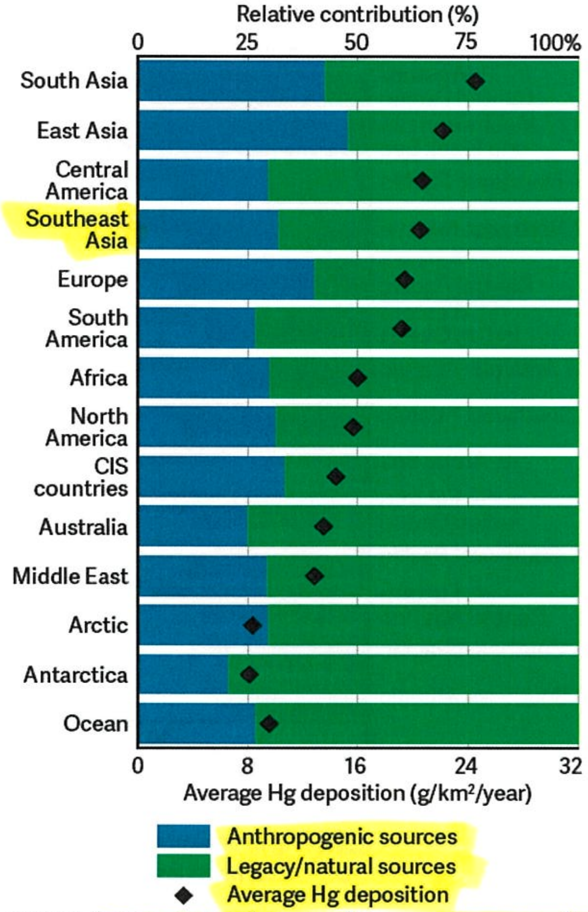


Figure 3. Average mercury deposition flux over various geographical regions in 2013 and the relative contribution of anthropogenic and natural/legacy source types to deposition as simulated by the chemical transport model ensemble.

The main pathway of human exposure to mercury is through fish consumption (Mahaffey et al., 2004, 2009; Sunderland et al., 2010). Mercury enters marine and freshwater ecosystems through direct anthropogenic releases, atmospheric deposition, riverine run-off and other pathways. In water bodies and bottom sediments inorganic mercury is converted by biotic and/or abiotic processes to methylmercury, a highly toxic organic form of mercury which accumulates and biomagnifies in aquatic food webs (Wiener et al., 2003; Sunderland et al., 2004, 2009, 2010; Cossa et al., 2009). It has been suggested that most methylmercury accumulating in ocean fish is derived from in situ methylmercury production within the upper waters, with the main source of mercury in the open ocean being atmospheric deposition (Mason et al., 2012). To estimate mercury loads to different aquatic regions and so connect these with potential accumulation in fish, mercury deposition has been calculated for the major fishing areas according to the classification of the UN Food and Agriculture Organization (FAO, 2014a). It should be noted that these rough estimates do not reflect the chain of processes leading to the accumulation of mercury in fish (aquatic chemistry, methylation, movement through the trophic web etc.) but rather indicate aquatic regions with the potential risk of fish contamination by mercury.

Figure 4a shows the spatial distribution of the ensemble mean annual mercury deposition over the ocean in 2013 in relation to the FAO Major Fishing Areas (specifications of the fishing

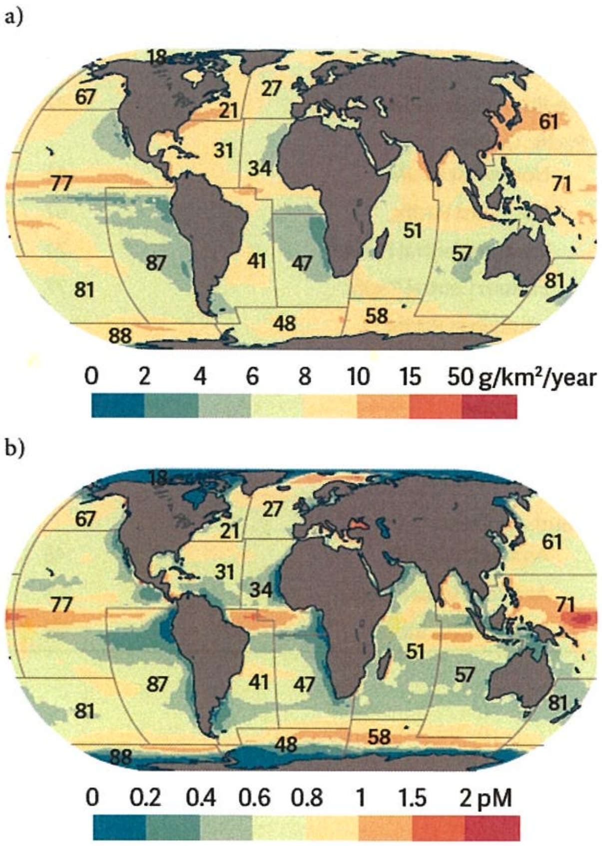


Figure 4. Spatial distribution of ensemble mean annual mercury deposition over the ocean in 2013 (a) and total mercury concentration in seawater simulated by GEOS-Chem (b). Lines show the FAO Major Fishing Areas (FAO, 2014a).

areas are given in Table 1). The global distribution of total mercury concentration in seawater simulated by one of the models (GEOS-Chem) is shown in Figure 4b. The highest deposition fluxes are over the Northwest Pacific (area 61), Northwest Atlantic (area 21), Western Central Atlantic (area 31) and Western Central Pacific (area 71). Significant fluxes are also detected over the Antarctic Indian Ocean (area 58) and Antarctic Pacific (area 88). The simulated pattern of mercury concentration in seawater generally follows the deposition distribution. The highest concentrations are characteristics of the equatorial parts of the Atlantic and Pacific Oceans, the Northeast Atlantic, and some areas of the Southern Ocean. High concentrations are also obtained for the Mediterranean and Black Sea.

Figure 5 shows annual mercury deposition and concentration in seawater averaged over the FAO Major Fishing Areas. The graphic also includes the total annual marine capture fisheries production according to FAO statistics for 2012 (FAO, 2014b). The largest total capture production takes place in the Northwest Pacific (area 61), Western Central Pacific (area 71) and Northeast Atlantic (area 27). These areas are also characterized by significant mercury deposition (10–15 g/km^2/y on average). The mercury concentration in some locations of these aquatic areas reaches maximum values (more than 1.5 pM). Total fisheries production is also significant in the Southeast Pacific (area 87) and the Eastern Indian Ocean (area 57), where atmospheric mercury deposition and seawater concentration are both relatively low.

Table 1. Specification of the FAO Major Fishing Areas (FAO, 2014a)

Fishing area	Code
Atlantic Ocean	
Northwest Atlantic	21
Northeast Atlantic	27
Western Central Atlantic	31
Eastern Central Atlantic	34
Southwest Atlantic	41
Southeast Atlantic	47
Arctic Sea	18
Mediterranean and Black Seas	37
Pacific Ocean	
Northwest Pacific	61
Northeast Pacific	67
Western Central Pacific	71
Eastern Central Pacific	77
Southwest Pacific	81
Southeast Pacific	87
Indian Ocean	
Western Indian Ocean	51
Eastern Indian Ocean	57
Southern Ocean	
Antarctic Atlantic	48
Antarctic Indian Ocean	58
Antarctic Pacific	88

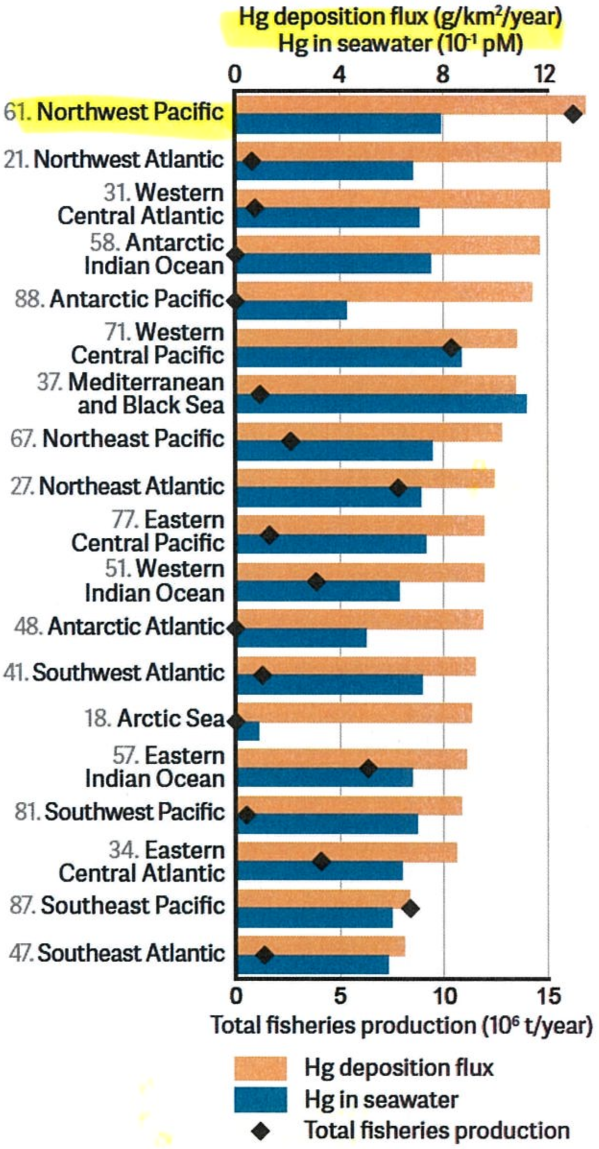


Figure 5. Average annual mercury deposition and total mercury concentration in the FAO Major Fishing Areas in 2013. Total annual marine capture fisheries production in 2012 is given for the same areas for comparison (FAO, 2014b).

3. Estimates of mercury intercontinental transport

Source apportionment of mercury deposition, illustrating atmospheric transport of mercury between different continents and regions, was evaluated by the three models. The definition of source and receptor regions adopted in the study is shown in Figure 6. The regions considered include the continents (Europe, North, Central and South America, Africa, Australia), large sub-continents (Middle East, countries of the Commonwealth of Independent States (CIS), South, East and Southeast Asia) and the Polar Regions (Figure 6a). The total anthropogenic emission of mercury from the selected geographical regions is shown in Figure 6b. The largest anthropogenic emissions are estimated for East Asia (616 t/y) and Africa (329 t/y). Considerable emissions (120–170 t/y) are also estimated for South America, Southeast and South Asia, and Central America. The smallest emissions are characteristics of Australia, Middle East and the Arctic (AMAP/UNEP, 2013).

As previously mentioned, mercury deposition in all regions consists of a contribution from contemporary anthropogenic emissions and a large contribution from natural/legacy sources. The former includes deposition from domestic emissions and mercury transported into the region from sources located in other regions. A comparison of the relative contributions of domestic and foreign anthropogenic sources to total mercury deposition in various regions as simulated by the model ensemble is illustrated in Figure 7. The share of domestic sources varies from zero in Antarctica to 36% in East Asia. In most regions (except for East Asia) the contribution of foreign sources is within the range 15–30%. In general, this agrees well with conclusions drawn in GMA 2013 (AMAP/UNEP 2013). In two regions (East and South Asia) the contribution of domestic sources (25–36%) exceeds the contribution of sources located outside the region (12–18%). This is due to significant anthropogenic emissions in these regions and to the dominant role played by emissions from industrial and combustion sources. Emissions from these sources contain an essential fraction of oxidized mercury, which mostly deposits within the region (Chapter). In Europe, both domestic and foreign emissions contribute almost equally (20%) to total mercury deposition. It should be noted that the models differ somewhat in their estimates of the relative contribution of domestic and foreign sources to average mercury deposition (Annex B, Figure B-4). The main reason for this is the difference in chemical speciation of anthropogenic emissions used by the models.

Some large contributors to global mercury emission – Africa, South America and Southeast Asia – are characterized by a considerably lower contribution of domestic sources (6–11%). This can be explained by the considerable portion of emissions from ASGM in these regions, which contain mercury in gaseous elemental form. The majority of these emissions contribute to global transport rather than deposition within the region. The lowest contributions of domestic sources were estimated for the Middle East (3%), Australia (2%) and the Arctic (1%), which are characterized by the lowest anthropogenic emissions

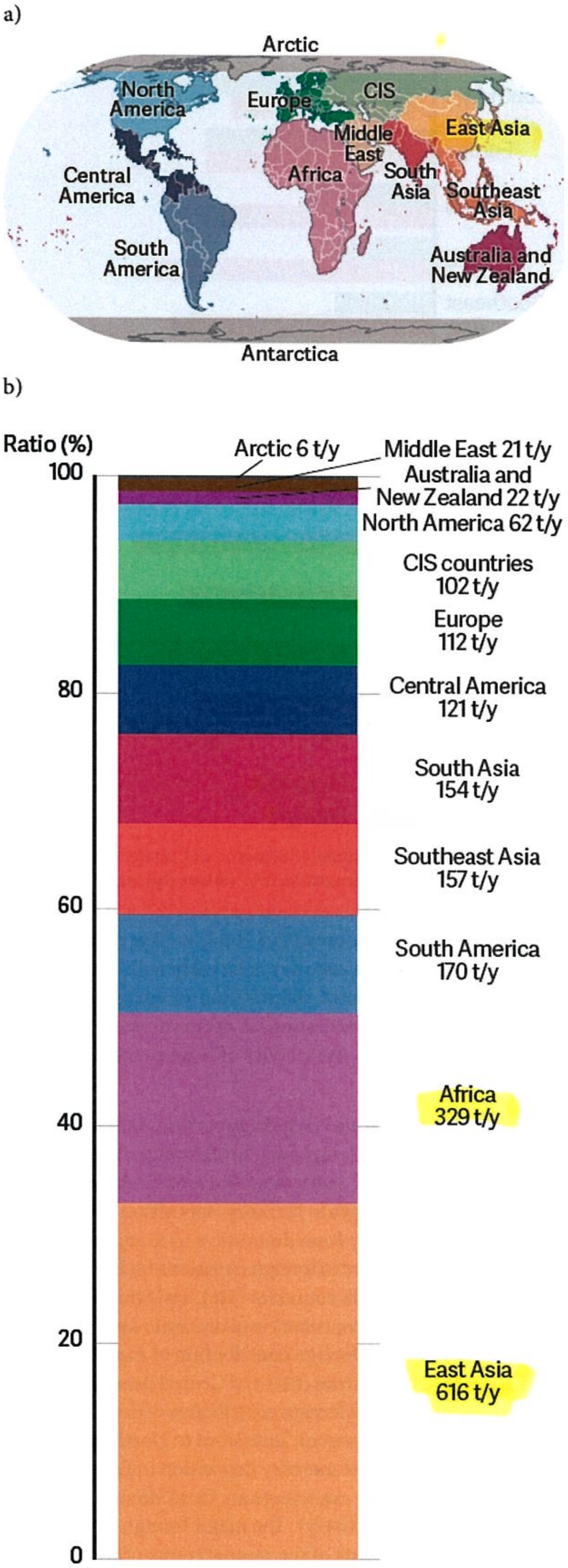


Figure 6. Definition of source and receptor regions used in the analysis (a) and the share of global anthropogenic mercury emissions among the source regions (b).

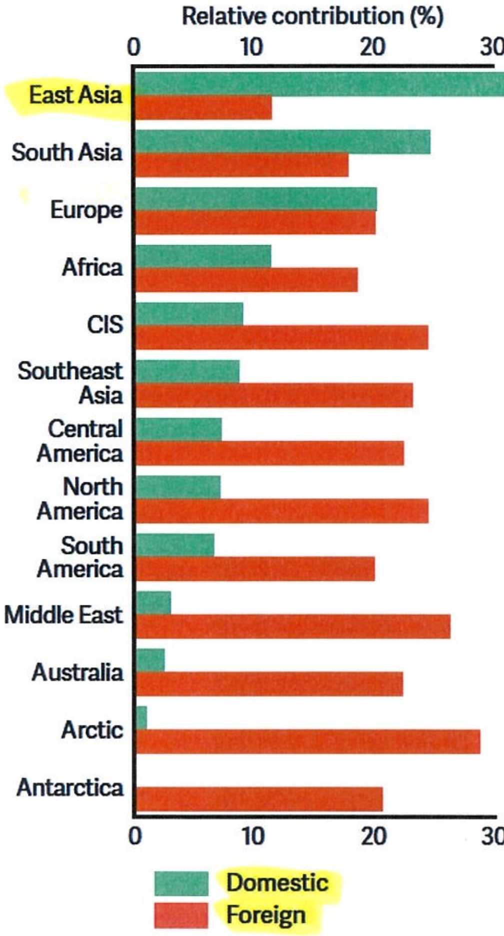


Figure 7. Relative contribution of domestic and foreign anthropogenic sources to total mercury deposition over various regions.

(Figure 6b). It should be noted that above average characteristics of mercury deposition can vary noticeably within the regions due to the uneven spatial distribution of emission sources. In particular, the contribution of domestic sources can be significantly higher in the vicinity of large point sources and industrial areas.

Figure 8 presents a source region apportionment of mercury deposition from contemporary anthropogenic sources to various geographical regions of the world. As previously mentioned, anthropogenic mercury deposition to Europe is derived almost equally from domestic and foreign emissions. The largest contributors to foreign emissions include East Asia (20%), Africa (8%), CIS countries (5%), and South Asia (3%). In North America the contribution of domestic sources (23%) is even smaller than the foreign contribution of East Asia (32%). Africa (12%), CIS countries (6%) and Central America (6%) are among other significant foreign contributors of deposition from contemporary anthropogenic emissions to North America. In contrast, anthropogenic mercury deposition to East and South Asia is dominated by contributions from domestic sources (76% and 58%, respectively). The major foreign contribution to these regions consists of the mutual transport between the regions and the considerable contribution from Africa. Mercury deposition to remote regions such as the Arctic and Antarctica is determined by long-range atmospheric transport from the major source regions. The main contributors for both regions are East Asia and Africa. The Arctic is also affected by emission sources in Europe and the CIS countries, and Antarctica by South and Central Americas.

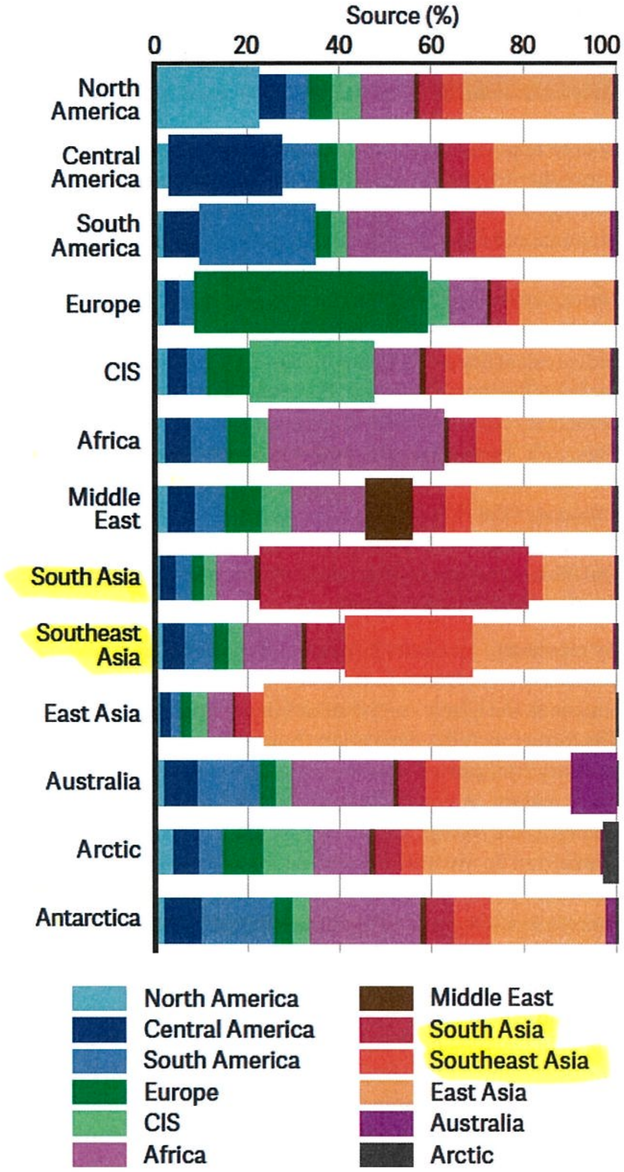


Figure 8. Source region apportionment of mercury deposition from contemporary anthropogenic emissions to various geographical regions in 2013.

Mercury deposition to aquatic regions is affected both by shoreline emission sources and by long-range atmospheric transport. Figure 9 shows East Asia to be the largest contributor to mercury deposition in almost all aquatic regions. Its contribution to mercury deposition from contemporary anthropogenic sources varies from 25% to 53%. It is followed by sources located in Africa (11–26%). The exception is the Mediterranean and Black Sea region, which is dominated by European emissions. As previously mentioned, the regions where considerable mercury deposition is accompanied by large total capture fisheries production include the Northwest Pacific, the Western Central Pacific and the Northeast Atlantic (Chapter 2). Anthropogenic mercury deposition in these regions is mostly determined by emissions from East Asia, Africa, Europe, CIS countries, South and Southeast Asia.

Both the absolute and relative contributions of different source regions to mercury deposition vary over the year. Figure 10 presents the model ensemble mean seasonal variation of source region apportionment of mercury deposition to the various geographical regions in 2013. Seasonal variation of deposition from domestic sources is considerably less than that from foreign and natural/legacy sources. Particularly in Europe, the CIS countries, North and Central Americas (Figs. 10a–d). It should be noted that temporal variation of direct anthropogenic emissions is not taken into account in the study. Given that local and regional mercury deposition is largely caused by removal of directly emitted oxidized mercury forms (GOM and PBM), variation of deposition from domestic sources is mostly determined by changes in the environmental conditions affecting removal processes (precipitation amount, stability of atmospheric boundary layer, vegetation height etc.).

In contrast, the deposition of mercury transported from other regions is highly affected by oxidation chemistry, which converts GEM transported in the atmosphere to GOM and PBM deposited to the ground by wet removal and surface uptake. Therefore, the contribution of foreign sources is greater in summer when mercury oxidation is more intensive. In the case of natural and legacy sources, the seasonal pattern is also affected by the intensity of mercury evasion from the surface. During the warm season, natural and legacy emission of mercury are greater due to higher temperatures and solar radiation as well as to the absence of snow cover. Seasonal variation of mercury deposition is also pronounced in southern hemisphere regions (South America and Australia) with maximum deposition in summer and minimum deposition in winter (Figs. 10g–h). Deposition in the Arctic and Antarctica has pronounced maximums in spring, due to intensive mercury oxidation and removal during AMDEs (Figs. 10i–j).

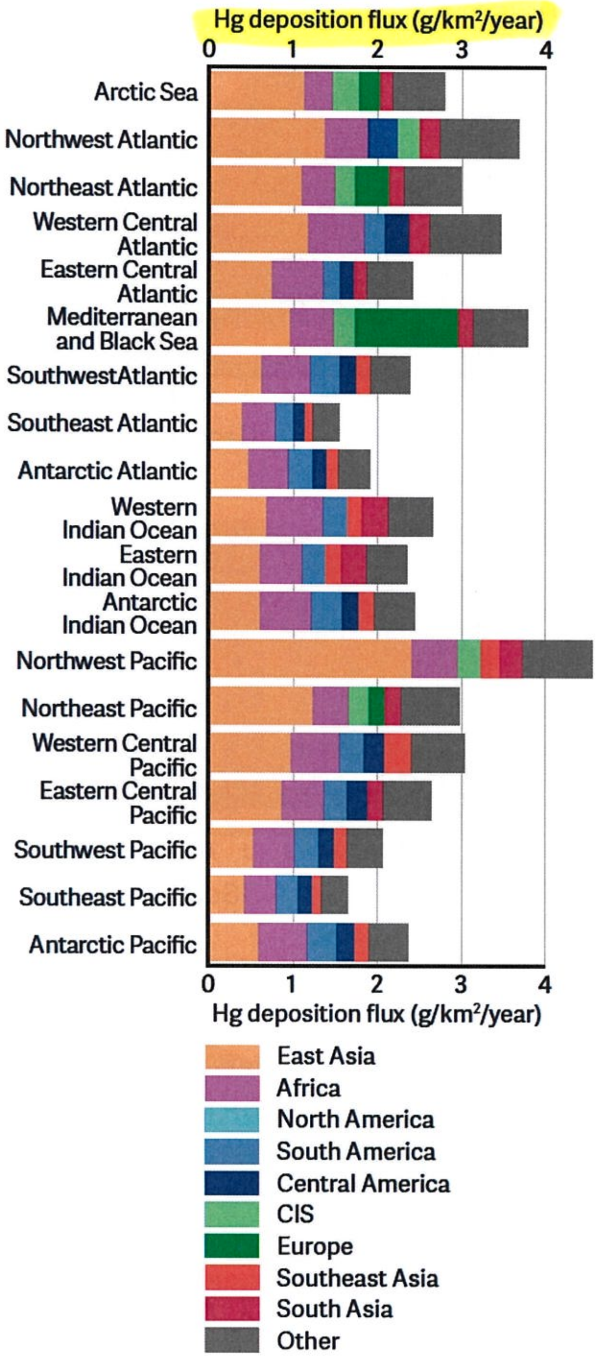
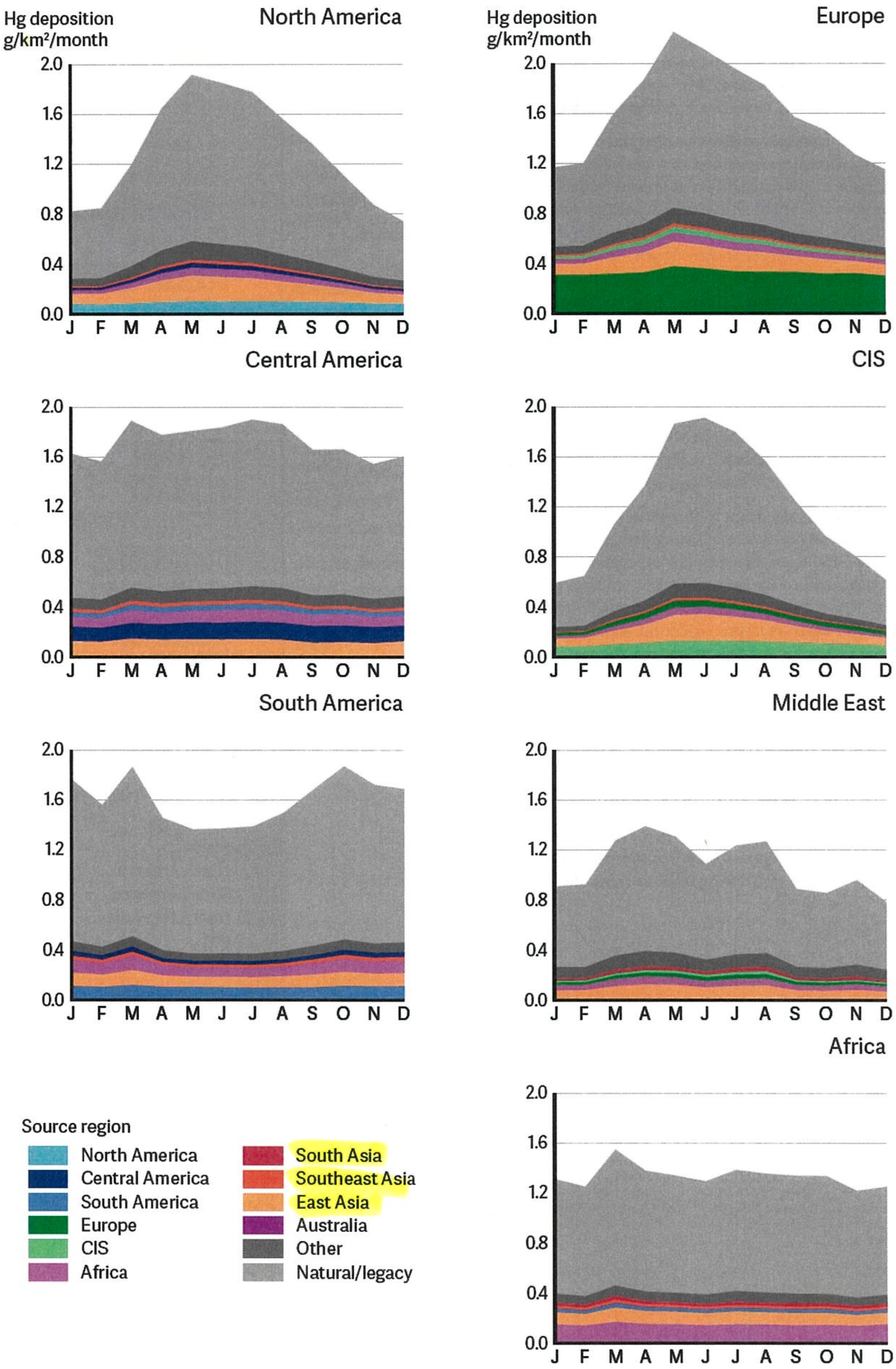


Figure 9. Source region apportionment of mercury deposition from contemporary anthropogenic sources to various aquatic regions in 2013


Hg deposition
g/km²/month
North America
Europe
Central America
CIS
South America
Middle East
Africa
0.0
0.4
0.8
1.2
1.6
2.0
J F M A M J J A S O N D
Source region
North America
Central America
South America
Europe
CIS
Africa
South Asia
Southeast Asia
East Asia
Australia
Other
Natural/legacy

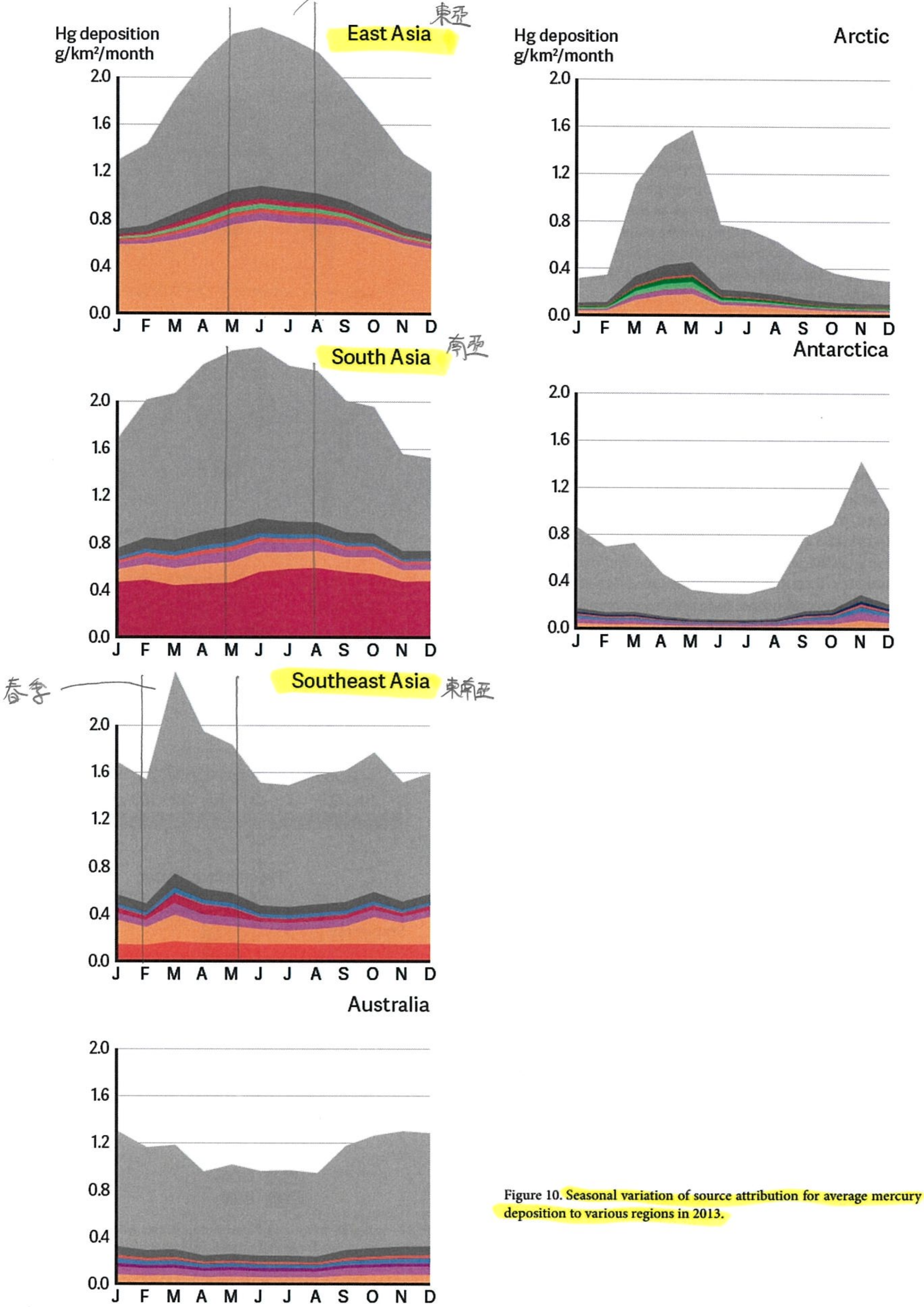


Figure 10. Seasonal variation of source attribution for average mercury deposition to various regions in 2013.

4. Mercury deposition from different emission sectors

The model ensemble was also applied for simulating mercury deposition from different anthropogenic emissions sectors. The sectors of mercury anthropogenic emissions were aggregated into three general groups in this subset: stationary combustion sources including power plants and distributed heating; industrial sources including stationary combustion for industry; intentional use and product waste associated sectors including ASGM.

A more detailed description of the emission sector groups is given in Table B-4 of Annex B. The spatial distribution of mercury emissions from the sector groups is shown in Figure 11. The majority of emissions from stationary combustion sources are located in the largest industrial and populated regions of the northern hemisphere – East and South Asia, Europe and North America – as well as in southern Africa in the southern hemisphere (Figure 11a). Emissions from industrial sources are more widely scattered than for stationary combustion sources (Figure 11b). South America, Sub-Saharan Africa and East and Southeast Asia are responsible for a significant proportion of mercury emissions from intentional use and product waste (Figure 11c). Total mercury emissions are 379, 642 and 854 t/y for stationary combustion, industrial sources and intentional use and product waste, respectively.

The chemical speciation of mercury emissions differs considerably between different sector groups (Figure 11d). According to the applied inventory (AMAP/UNEP, 2013; AMAP, 2014), emissions from stationary combustion consist of approximately equal contributions of elemental mercury (GEM) and oxidized forms (GOM, PBM). The proportion of oxidized mercury is much smaller in emissions from industrial sources (20%). More than 95% of mercury emissions from intentional use and product waste are in the elemental gaseous form. However, estimates of mercury emissions speciation are associated with significant uncertainties (Amos et al., 2012; Zhang et al., 2012; Kos et al., 2013) and this can affect the results of the analysis.

Simulated global patterns of the relative contributions of the three sector groups to total mercury deposition are shown in Figure 12. The impact of stationary combustion sources is mostly limited to the large industrial regions in East and South Asia, Europe, the eastern part of North America and South Africa, where the contribution of this sector group exceeds 20–30% of total mercury deposition (Figure 12a). In contrast, the contribution of stationary combustion sources is below 10% in other regions. The spatial difference is determined by the significant proportion of short-lived oxidized mercury forms in emissions from this sector group, and leads to strong mercury deposition in the vicinity of the source regions. Emissions from industrial sources affect the whole northern hemisphere, where the contribution to deposition of this sector group exceeds 10% (Figure 12b). Mercury released from intentional use and product waste (mostly as GEM) can be transported globally.

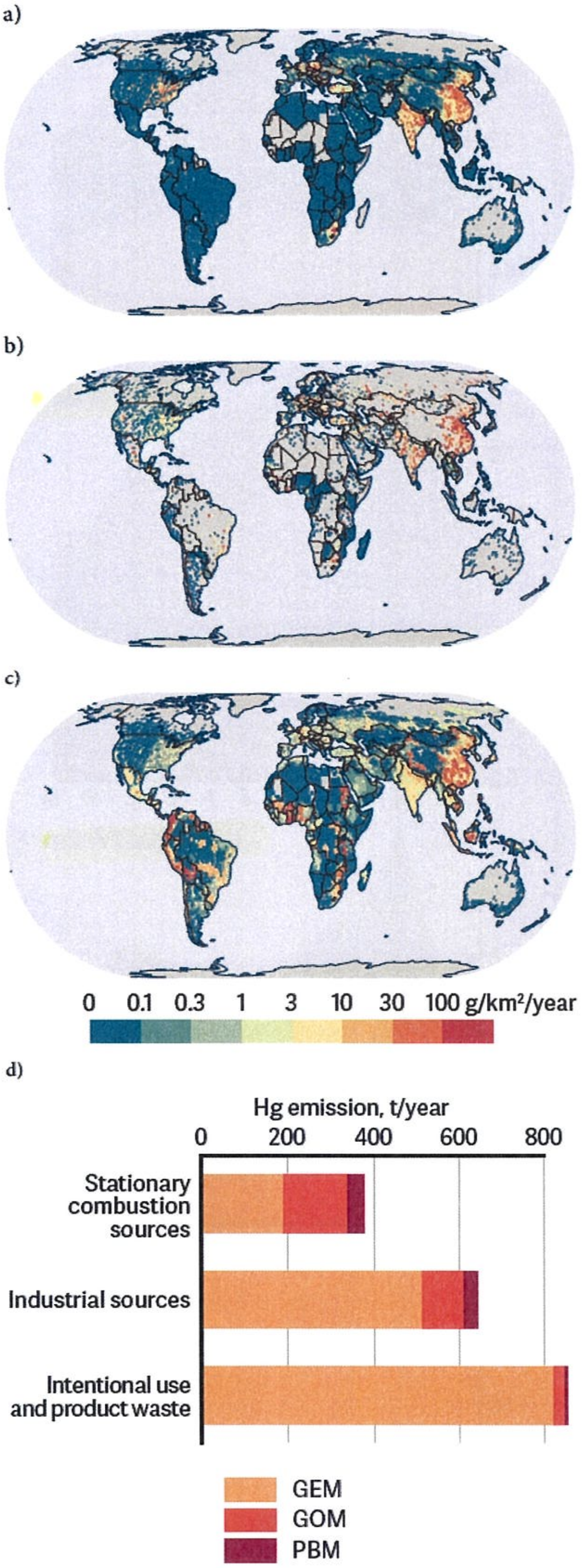


Figure 11. Spatial distribution of mercury emissions from stationary combustion sources (a), industrial sources (b) and intentional use and product waste (c). The chemical speciation of mercury emissions from the three sector groups is shown in 'd'.

The contribution of this sector group varies between 10% and 30% everywhere with the maximum impact occurring in the equatorial zone (Figure 12c).

The sectoral composition of mercury deposition in different geographical regions is illustrated in this figure. It is clear that anthropogenic mercury deposition in the major source regions is largely determined by stationary combustion and industrial sources. These emission sectors dominate in Asia, Europe, North America and the CIS countries. In contrast, regions with lower emissions (Central and South America, Australia and New Zealand, the Arctic etc.) are more affected by mercury from intentional use and product waste associated sectors.

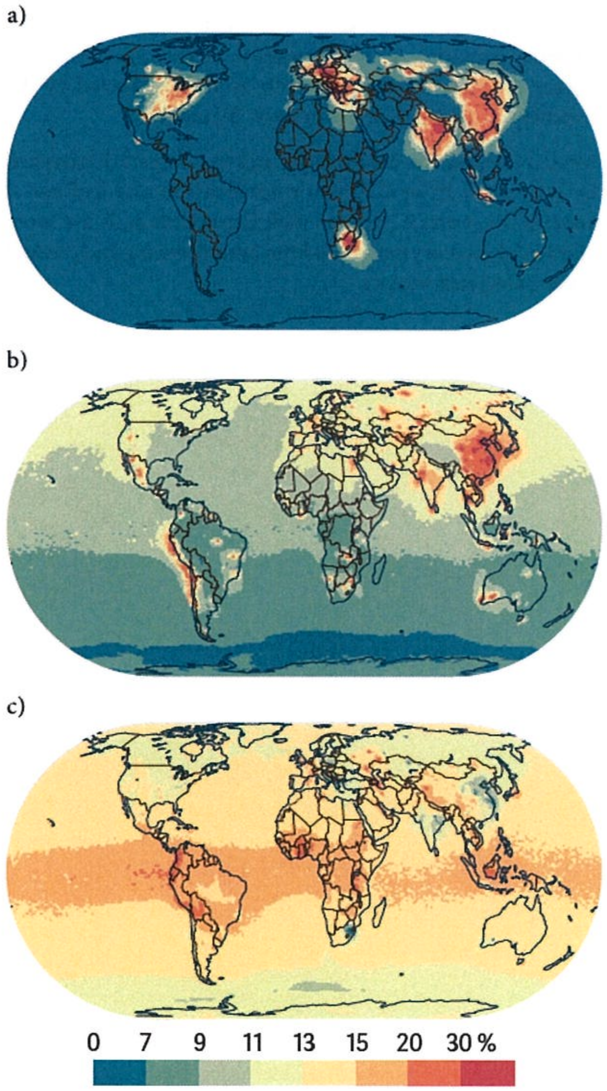


Figure 12. Ensemble mean relative contribution of different groups of emission sectors to total mercury deposition in 2013: stationary combustions sources (a), industrial sources (b) and intentional use and product waste (c).

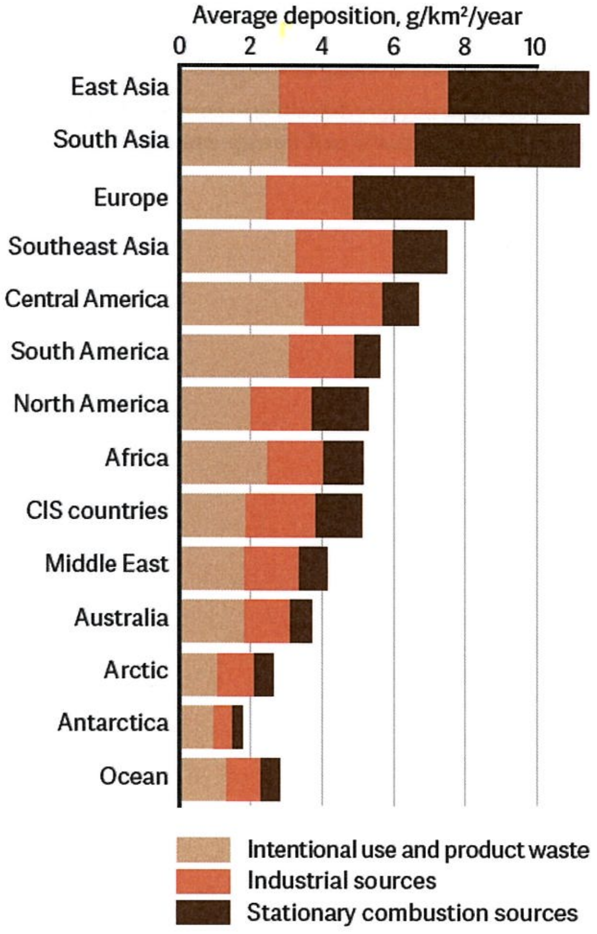


Figure 13. Contribution of mercury emissions from the three sector-specific emission groups to average mercury deposition from contemporary anthropogenic sources in various geographic regions in 2013 as simulated by the model ensemble.

5. Conclusions

The major conclusions of this assessment of mercury atmospheric dispersion and deposition on a global scale and the intercontinental transport and source apportionment of mercury deposition, based on simulation results from an ensemble of global-scale models, may be summarized as follows.

High mercury deposition fluxes are characteristic of the large industrial regions (East and South Asia, Europe, North America etc.) and regions with significant mercury emissions from ASGM (Southeast Asia, Central and South America, Sub-Saharan Africa). Relatively large deposition is also detected over some remote areas of the oceans and in the polar regions.

Mercury deposition in all geographical regions comprises a contribution emitted from the regions' domestic sources, mercury transported into the region from sources located in other regions ('foreign sources'), and a significant contribution from natural and legacy sources. The share of current anthropogenic emissions varies between 20% and 50%. The contribution of natural/legacy sources is generally greater in remote regions with lower atmospheric deposition.

The contribution of domestic sources varies from zero (Antarctica) to 36% (East Asia). In all regions the contribution of foreign sources is within the range 12–30%.

Anthropogenic mercury deposition in Europe is derived almost equally from domestic and foreign emissions. The largest contributors to foreign emissions include East Asia (20%), Africa (8%), CIS countries (5%), and South Asia (3%). The contribution of domestic sources to mercury deposition in North America (23%) is smaller than total contribution from other source regions, the largest of which include East Asia (32%), Africa (12%), CIS countries (6%) and Central America (6%). In contrast, deposition of mercury to East and South Asia is dominated by contributions from domestic sources (76% and 58%, respectively).

Oceanic regions characterized both by significant mercury deposition and by the highest total capture fisheries production include the Northwest Pacific, Western Central Pacific and Northeast Atlantic. Mercury deposition in these regions is mostly determined by emissions from East Asia, Africa, Europe, CIS countries, and South and Southeast Asia.

The simulated seasonal variation in mercury deposition from domestic sources is considerably less than that from foreign and natural/legacy sources and is mostly determined by changes in environmental conditions affecting removal processes. The contribution of foreign sources is greater in summer when mercury oxidation is more intensive. In the case of natural/legacy sources, the seasonal pattern is also affected by the intensity of mercury emission from the surface.

Mercury deposition in industrial regions is largely determined by emissions from stationary combustion and industrial sources. In contrast, regions with lower emissions are more affected by mercury emissions from intentional use and product waste associated sectors.

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Annex A. Model ensemble

Table A-1. Characteristics of chemical transport models participated in the multi-model experiments.

Characteristics	**GMHG**[a]	**GEOS-Chem**	**GLEMOS**
Institution	Environment Canada	Massachusetts Institute of Technology	Meteorological Synthesizing Centre - East
Domain	Global	Global	Global
Spatial resolution			
Horizontal	1° × 1°	2.5° × 2°	1° × 1°
Vertical	58 levels, top 7 hPa	47 levels, top 0.01 hPa	20 levels, top 10 hPa
Type	Atmospheric	Multi-media	Atmospheric
Emissions			
Anthropogenic, t/y	1875	1875	1875
Speciation (average), GEM : GOM : PBM	96 : 3 : 1	81 : 19 : 0	81 : 15 : 4
Natural and legacy, t/y	3660	5070	3995
Atmospheric chemistry			
Oxidation (air)	OH	Br	OH, O3, Cl2
Reduction (air)	none	none	none
Oxidation (cloud water)	none	none	OH, O3, HOCl/OCl-
Reduction (cloud water)	none	none	SO32-
Remarks	Parameterization of AMDEs based on Br chemistry, re-emission from snow	Gas-particle partitioning of Hg(II). Parameterization of AMDEs based on Br chemistry, re-emission from snow	Parameterization of AMDEs based on Br chemistry, re-emission from snow, chemical reactants imported from MOZART and p-TOMCAT
References	Durnford at al. (2012); Kos et al. (2013); Dastoor et al. (2015)	Holmes et al. (2010); Amos et al. (2012)	Travnikov et al. (2009)

[a] GMHG is a new chemical transport model for mercury that is based on the GRAHM model developed by Environment Canada.

Annex B. Simulation results for the individual chemical transport models

B.1. Spatial distribution of mercury air concentrations and deposition

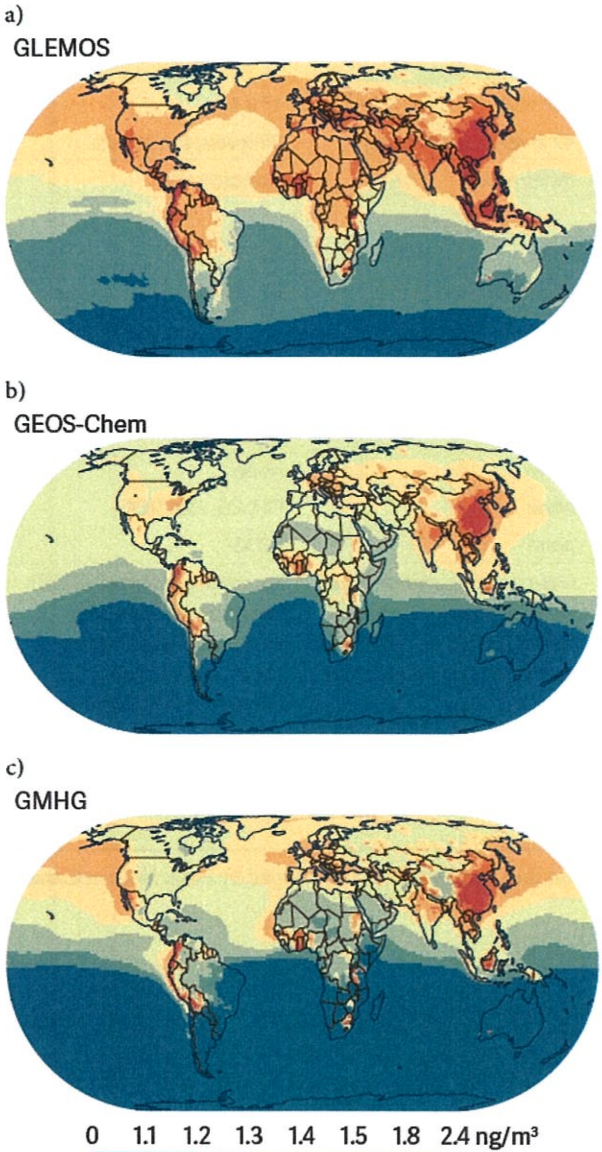


Figure B-1. Spatial distribution of annual mean gaseous elemental mercury (GEM) concentration in ambient air in 2013 as simulated by the three chemical transport models.

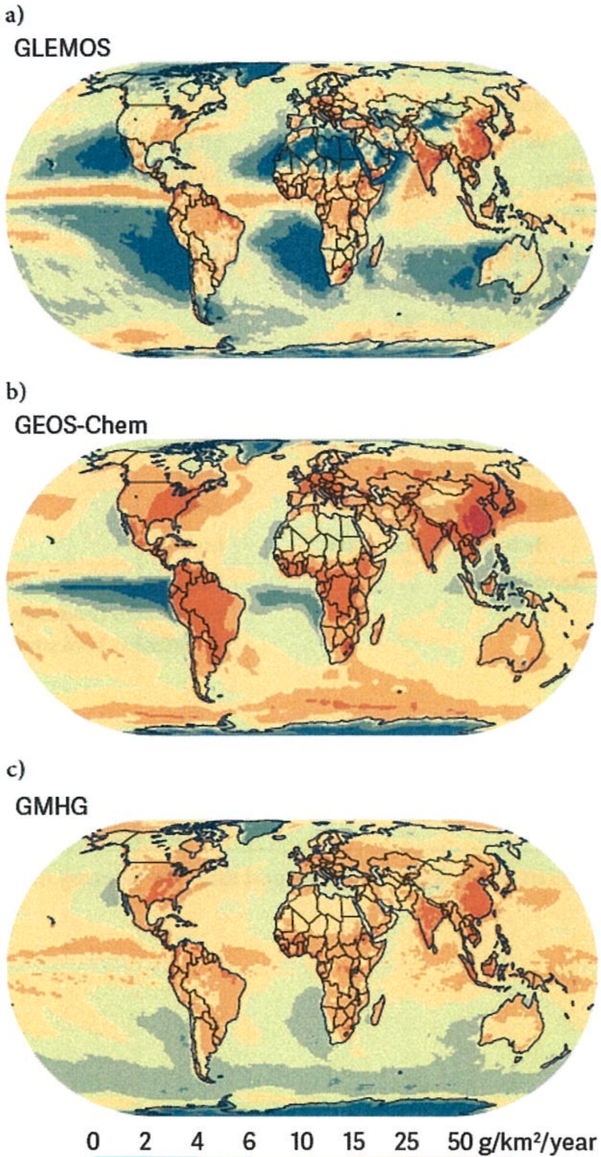


Figure B-2. Spatial distribution of total mercury (dry and wet) deposition in 2013 as simulated by the three chemical transport models.

B.2. Source attribution for atmospheric mercury deposition

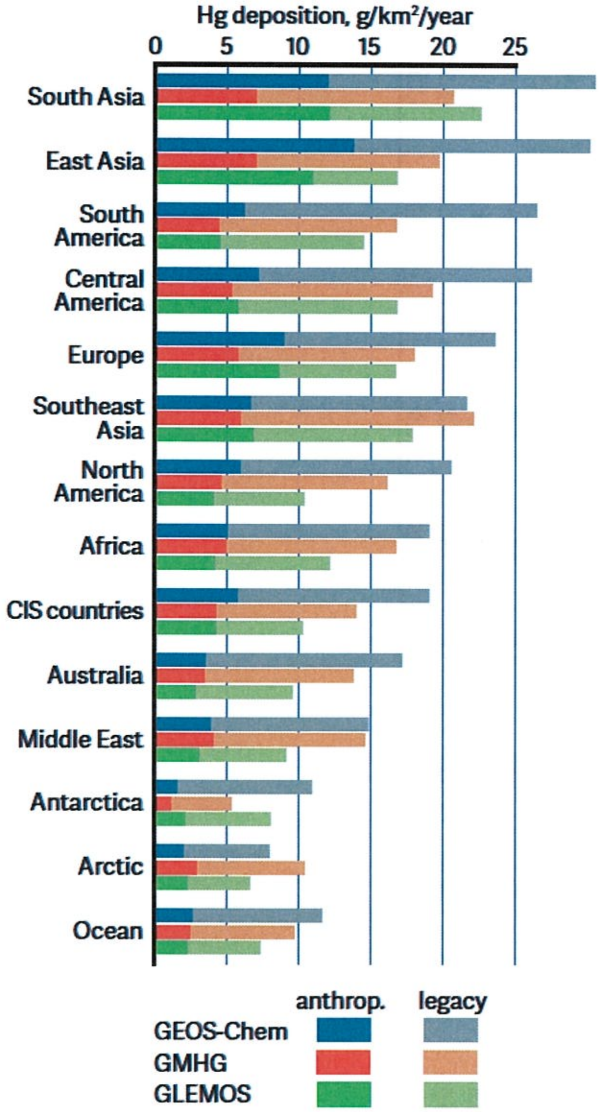


Figure B-3. Average mercury deposition flux in various geographical regions in 2013 as simulated by the three chemical transport models.

Table B-1. Nomenclature of sources and receptors

	Code	Description
Terrestrial regions	NAM	North America
	EUR	Europe
	SAS	South Asia
	EAS	East Asia
	SEA	Southeast Asia
	PAN	Australia and New Zealand
	AFR	Africa
	MDE	Middle East
	MCA	Central America
	SAM	South America
	CIS	CIS countries
	ARC	Arctic
	ANT	Antarctic
Aquatic regions	ARS	Arctic Sea
	MED	Mediterranean and Black Seas
	ATL	Atlantic Ocean
	PAC	Pacific Ocean
	IND	Indian Ocean
	STH	Southern Ocean
	NAT	Natural / legacy sources

Table B-2. Source-receptor deposition matrix simulated by GLEMOS, tonnes/year

	Area, km²	NAM	EUR	SAS	EAS	SEA	PAN	AFR	MDE	MCA	SAM	CIS	ARC	NAT	Total
Deposition to terrestrial regions															
NAM	1.69×10^7	**21.8**	3.0	3.1	18.4	3.7	0.3	7.3	0.5	4.1	3.2	3.5	0.3	105.4	174.6
EUR	5.53×10^6	0.7	**29.1**	1.2	7.0	1.5	0.1	3.4	0.3	1.2	1.3	1.9	0.1	44.5	92.3
SAS	5.07×10^6	0.6	1.2	**41.6**	7.1	1.9	0.2	3.9	0.6	1.5	1.8	1.4	0.1	52.6	114.4
EAS	1.16×10^7	0.8	1.7	3.1	**106.4**	3.2	0.2	4.6	0.4	1.8	2.0	2.8	0.2	67.5	194.7
SEA	4.94×10^6	0.5	1.0	2.5	8.9	**12.9**	0.2	3.6	0.2	1.4	1.9	1.1	0.1	54.0	88.2
PAN	8.06×10^6	0.4	0.8	1.3	5.4	2.1	**3.5**	4.4	0.2	1.6	2.7	0.9	0.1	53.5	76.9
AFR	3.00×10^7	2.3	6.2	6.9	28.5	8.4	1.0	**48.8**	1.7	6.8	9.5	5.0	0.4	238.1	363.6
MDE	5.17×10^6	0.4	1.4	1.0	4.3	1.0	0.1	2.6	**2.7**	0.9	1.0	1.0	0.1	30.7	47.1
MCA	5.21×10^6	1.0	1.2	1.5	7.5	2.0	0.2	4.8	0.3	**8.1**	2.4	1.3	0.1	57.2	87.7
SAM	1.53×10^7	1.2	2.6	3.7	16.1	5.4	0.7	13.4	0.6	5.4	**18.2**	2.7	0.2	151.1	221.3
CIS	1.79×10^7	1.7	6.7	3.1	21.1	3.6	0.4	7.4	0.9	3.0	3.2	**25.2**	0.6	107.3	184.1
ARC	2.24×10^7	1.7	4.3	2.9	18.6	3.4	0.3	6.9	0.6	2.8	3.0	5.2	**1.8**	97.5	148.9
ANT	3.42×10^7	1.4	3.1	4.4	19.2	7.1	1.5	16.2	0.7	5.7	10.8	3.2	0.2	202.5	276.0
Deposition to aquatic regions															
ARS	9.25×10^6	0.8	1.5	1.1	7.1	1.3	0.1	2.6	0.2	1.1	1.1	1.9	0.4	36.8	55.9
MED	2.99×10^6	0.2	3.3	0.3	1.7	0.4	0	1.3	0.2	0.3	0.3	0.5	0	11.4	20.2
ATL	8.53×10^7	8.8	13.6	11.5	59.1	15.1	1.7	37.5	2.0	13.6	18.3	11.3	1.1	428.2	621.9
PAC	1.69×10^8	9.2	18.8	24.2	149.2	39.5	5.1	68.6	3.9	28.7	40.3	21.9	1.8	883.7	1294.9
IND	6.06×10^7	2.3	5.0	17.8	32.4	12.6	3.0	26.8	1.8	8.2	13.5	5.2	0.4	283.1	412.3
STH	3.55×10^7	1.8	3.8	5.4	23.6	8.7	1.8	20.5	0.9	7.0	13.3	3.9	0.3	246.4	337.6

Table B-3. Source-receptor deposition matrix simulated by GEOS-Chem, tonnes/year

	Area, km²	NAM	EUR	SAS	EAS	SEA	PAN	AFR	MDE	MCA	SAM	CIS	ARC	NAT	Total
Deposition to terrestrial regions															
NAM	1.69×10^7	**25.0**	4.7	5.1	32.3	4.3	0.3	11.5	0.9	6.4	4.6	6.1	0.4	246.2	347.8
EUR	5.53×10^6	1.0	**26.3**	1.6	9.8	1.3	0.1	3.8	0.4	1.5	1.4	2.5	0.1	80.8	130.7
SAS	5.07×10^6	0.7	1.3	**36.8**	9.0	1.9	0.2	4.9	0.7	1.9	2.1	1.6	0.1	93.4	154.6
EAS	1.16×10^7	1.7	3.2	5.9	**122.1**	4.3	0.3	8.7	0.7	3.5	3.6	5.8	0.3	188.7	348.6
SEA	4.94×10^6	0.5	0.9	3.1	10.6	**9.5**	0.2	3.8	0.2	1.4	1.8	1.0	0.1	73.6	106.7
PAN	8.06×10^6	0.5	1.0	1.7	6.6	2.2	**3.0**	6.6	0.2	2.2	4.1	1.0	0.1	109.2	138.3
AFR	3.00×10^7	2.9	6.8	8.4	34.3	8.5	0.9	**62.2**	1.6	8.9	12.2	5.7	0.3	419.2	572.1
MDE	5.17×10^6	0.5	1.5	1.4	6.1	1.1	0.1	3.3	**2.2**	1.2	1.3	1.3	0.1	56.3	76.5
MCA	5.21×10^6	1.0	1.4	2.0	9.0	1.9	0.2	6.6	0.3	**10.7**	3.0	1.5	0.1	98.4	136.0
SAM	1.53×10^7	1.7	3.1	5.0	20.3	6.0	0.8	20.3	0.7	7.9	**26.4**	3.2	0.2	308.2	403.9
CIS	1.79×10^7	2.9	9.6	4.6	34.3	3.9	0.3	10.3	1.3	4.3	4.0	**28.7**	0.8	236.1	341.2
ARC	2.24×10^7	1.8	3.8	2.4	18.2	2.1	0.2	5.6	0.5	2.3	2.2	5.4	**1.6**	132.0	178.0
ANT	3.42×10^7	1.0	1.9	3.2	12.6	4.2	1.3	14.6	0.5	4.7	10.0	2.0	0.1	315.6	371.7
Deposition to aquatic regions															
ARS	9.25×10^6	0.7	1.3	0.9	6.6	0.7	0.1	2.0	0.2	0.8	0.8	1.9	0.4	47.7	64.0
MED	2.99×10^6	0.3	5.9	0.6	3.5	0.6	0	1.9	0.2	0.6	0.6	1.0	0	30.3	45.8
ATL	8.53×10^7	9.6	15.1	14.6	70.3	15.0	1.7	44.6	2.3	16.9	22.4	12.5	1.0	736.9	962.8
PAC	1.69×10^8	10.3	18.1	28.6	164.4	34.0	4.5	82.5	4.2	32.6	44.9	22.3	1.3	1437.8	1885.4
IND	6.06×10^7	2.9	5.3	20.4	36.5	12.3	2.8	37.7	2.0	11.4	18.6	5.7	0.3	530.1	686.1
STH	3.55×10^7	1.7	3.1	5.2	20.5	6.9	2.0	23.6	0.8	7.5	16.0	3.3	0.2	501.0	591.9

Table B-4. Source-receptor deposition matrix simulated by GMHG, tonnes/year

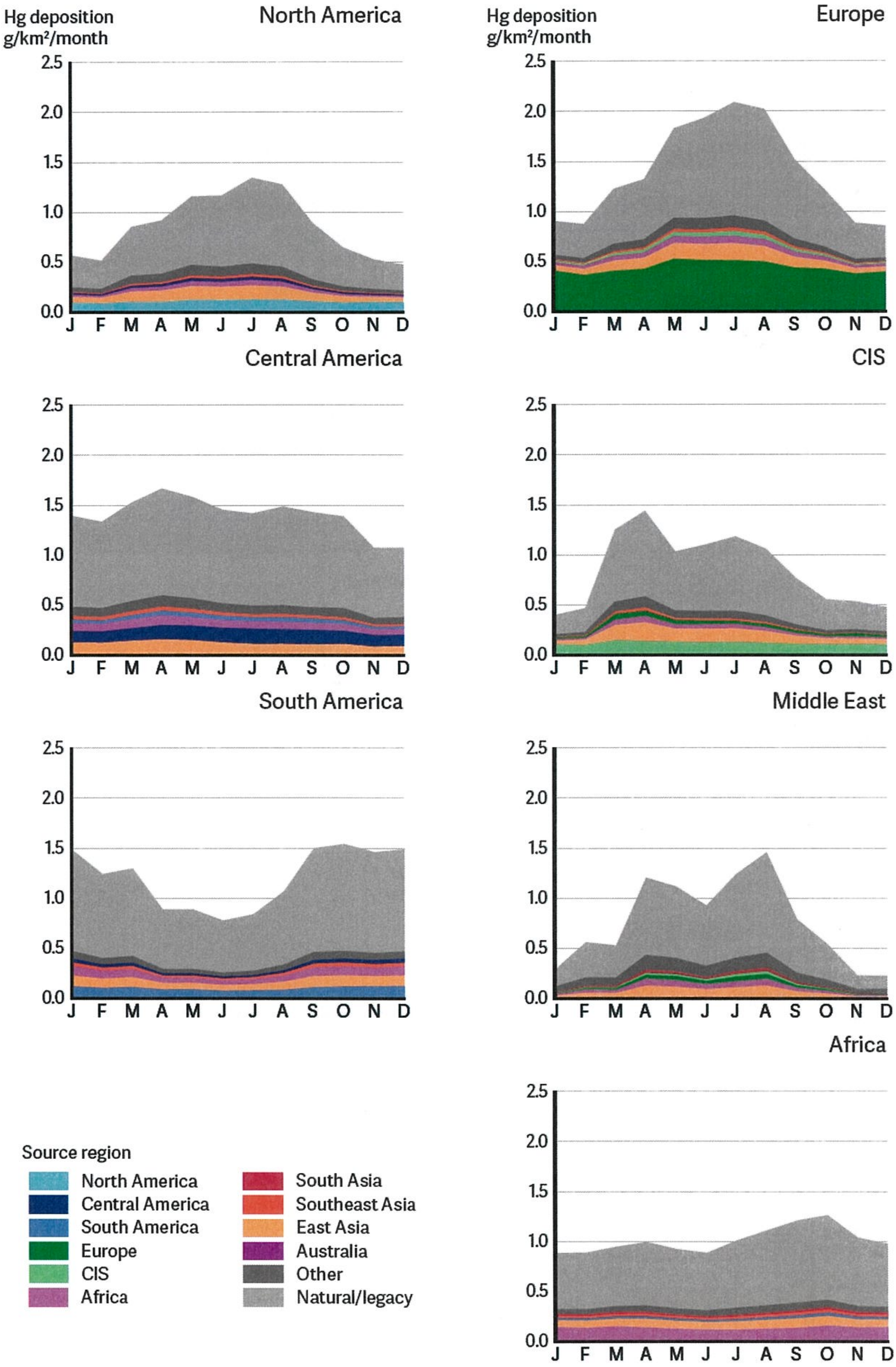
	Area, km²	NAM	EUR	SAS	EAS	SEA	PAN	AFR	MDE	MCA	SAM	CIS	ARC	NAT	Total
Deposition to terrestrial regions															
NAM	1.69×10^7	**10.0**	5.0	5.1	30.1	3.0	0.4	10.1	0.8	4.8	4.7	6.2	0.5	193.1	273.7
EUR	5.53×10^6	1.3	**9.9**	1.7	9.6	1.0	0.1	3.4	0.3	1.4	1.5	2.4	0.2	67.3	99.9
SAS	5.07×10^6	0.8	1.3	**14.2**	8.6	1.3	0.2	4.4	0.5	1.6	2.0	1.5	0.1	68.7	105.1
EAS	1.16×10^7	1.8	3.0	4.3	**52.7**	2.5	0.3	7.1	0.6	2.9	3.3	4.4	0.3	145.0	228.0
SEA	4.94×10^6	0.7	1.1	2.7	10.2	**4.2**	0.3	5.0	0.3	1.8	2.5	1.3	0.1	79.5	109.6
PAN	8.06×10^6	0.7	1.0	2.0	7.4	1.7	**1.5**	6.8	0.2	2.2	4.1	1.1	0.1	83.3	112.0
AFR	3.00×10^7	4.3	8.1	10.6	40.3	6.6	1.1	**52.5**	1.4	8.9	12.6	6.7	0.4	351.7	505.2
MDE	5.17×10^6	0.8	1.7	2.0	7.4	1.0	0.1	3.6	**1.0**	1.3	1.5	1.5	0.1	54.0	76.0
MCA	5.21×10^6	1.0	1.3	1.9	8.1	1.2	0.2	5.8	0.2	**4.7**	2.3	1.3	0.1	72.2	100.4
SAM	1.53×10^7	1.7	2.5	4.7	17.2	3.5	0.8	16.8	0.5	5.4	**13.8**	2.6	0.2	188.0	257.6
CIS	1.79×10^7	3.2	7.5	4.3	27.2	2.5	0.3	8.3	0.8	3.6	3.8	**16.1**	0.8	173.7	252.3
ARC	2.24×10^7	3.3	6.1	4.0	27.4	2.4	0.3	7.8	0.7	3.6	3.7	8.2	**1.6**	164.9	233.9
ANT	3.42×10^7	1.0	1.5	3.0	10.9	2.5	1.0	10.6	0.3	3.3	6.6	1.6	0.1	141.4	183.8
Deposition to aquatic regions															
ARS	9.25×10^6	2.0	3.5	2.3	15.8	1.3	0.1	4.4	0.4	2.1	2.1	4.8	0.8	91.8	131.3
MED	2.99×10^6	0.4	1.7	0.6	3.0	0.3	0	1.2	0.1	0.5	0.5	0.7	0	21.5	30.6
ATL	8.53×10^7	8.9	13.1	16.2	72.7	10.8	1.9	47.4	2.1	15.5	21.4	13.0	1.1	588.3	812.1
PAC	1.69×10^8	14.1	21.1	35.2	158.0	26.8	4.8	89.0	4.2	38.7	54.1	24.5	1.6	1258.4	1730.4
IND	6.06×10^7	4.0	6.2	16.4	43.8	9.5	2.3	35.8	1.6	11.2	18.5	6.4	0.4	416.6	572.6
STH	3.55×10^7	1.2	1.9	3.7	13.6	3.1	1.2	13.1	0.4	4.1	8.1	2.0	0.1	172.4	225.0


a) GLEMOS

b) GEOS-Chem

c)GMHG

Figure B-4. Relative contribution of domestic and foreign anthropogenic sources to average mercury deposition over various regions in 2013.


Hg deposition g/km²/month
North America
Hg deposition g/km²/month
Europe
Central America
CIS
South America
Middle East
Africa
2.5
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
Source region
North America
Central America
South America
Europe
CIS
Africa
South Asia
Southeast Asia
East Asia
Australia
Other
Natural/legacy

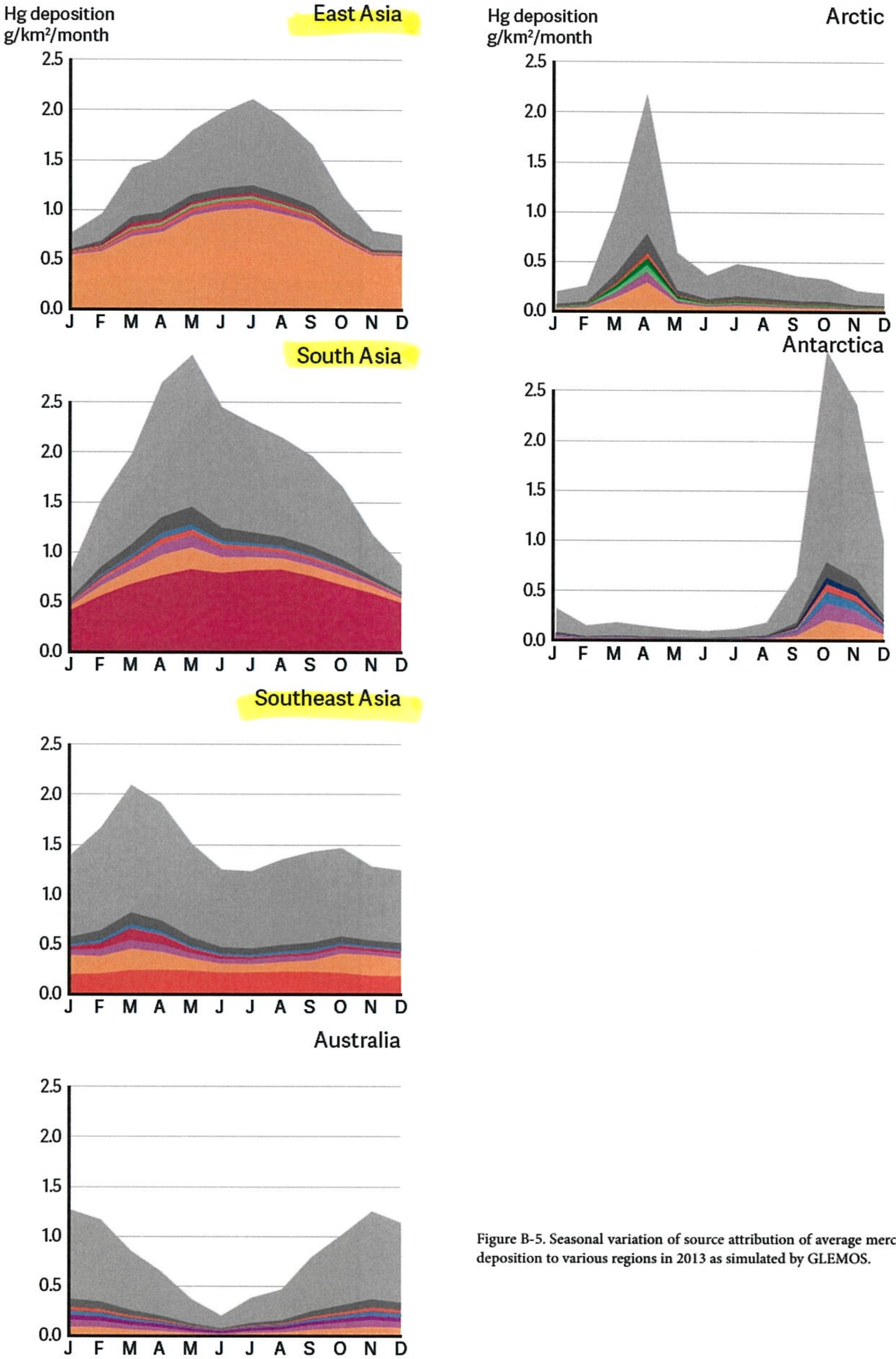
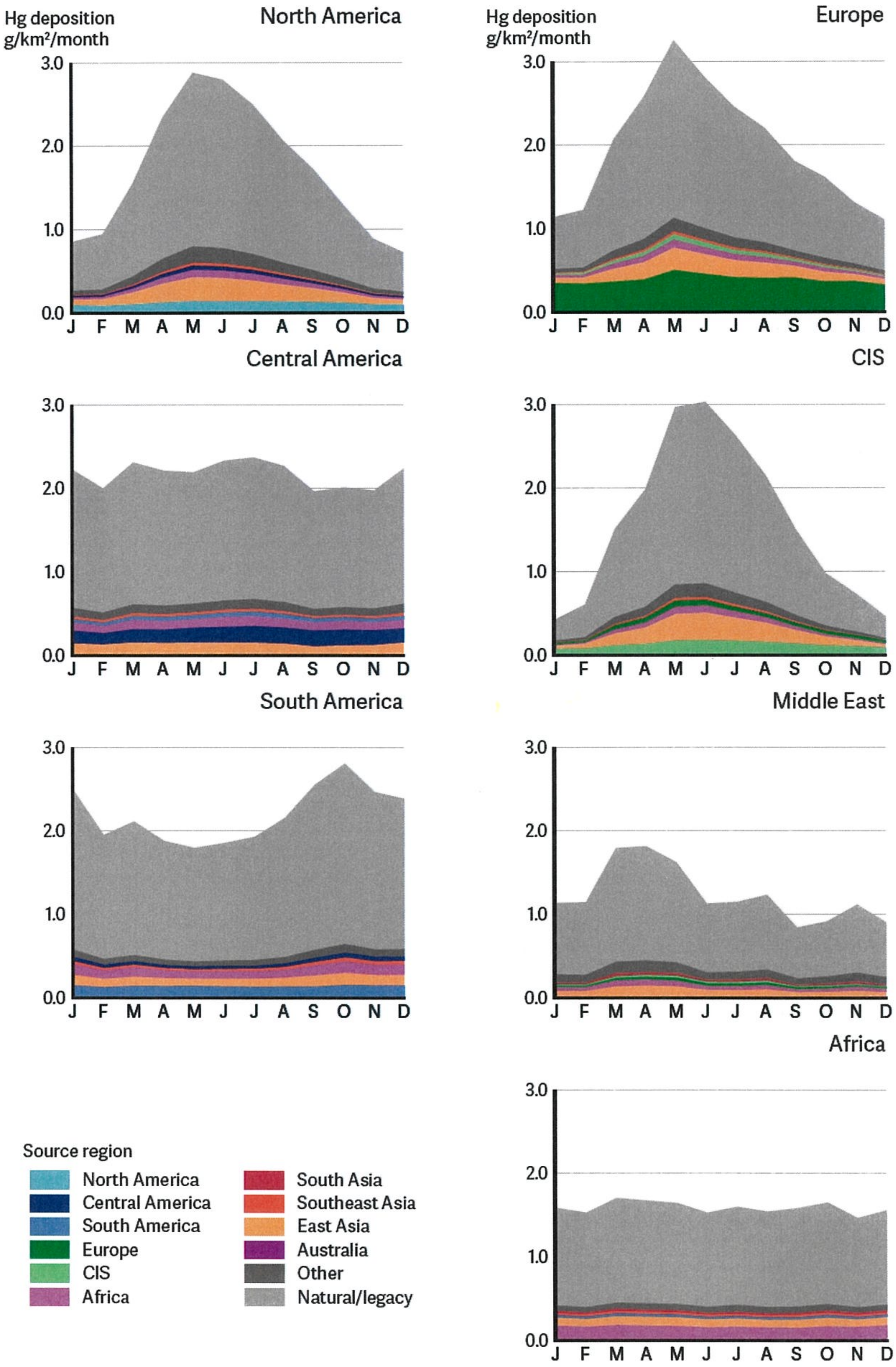


Figure B-5. Seasonal variation of source attribution of average mercury deposition to various regions in 2013 as simulated by GLEMOS.


Hg deposition g/km²/month
North America
Europe
Central America
CIS
South America
Middle East
Africa
3.0
2.0
1.0
0.0
J F M A M J J A S O N D
Source region
North America
Central America
South America
Europe
CIS
Africa
South Asia
Southeast Asia
East Asia
Australia
Other
Natural/legacy

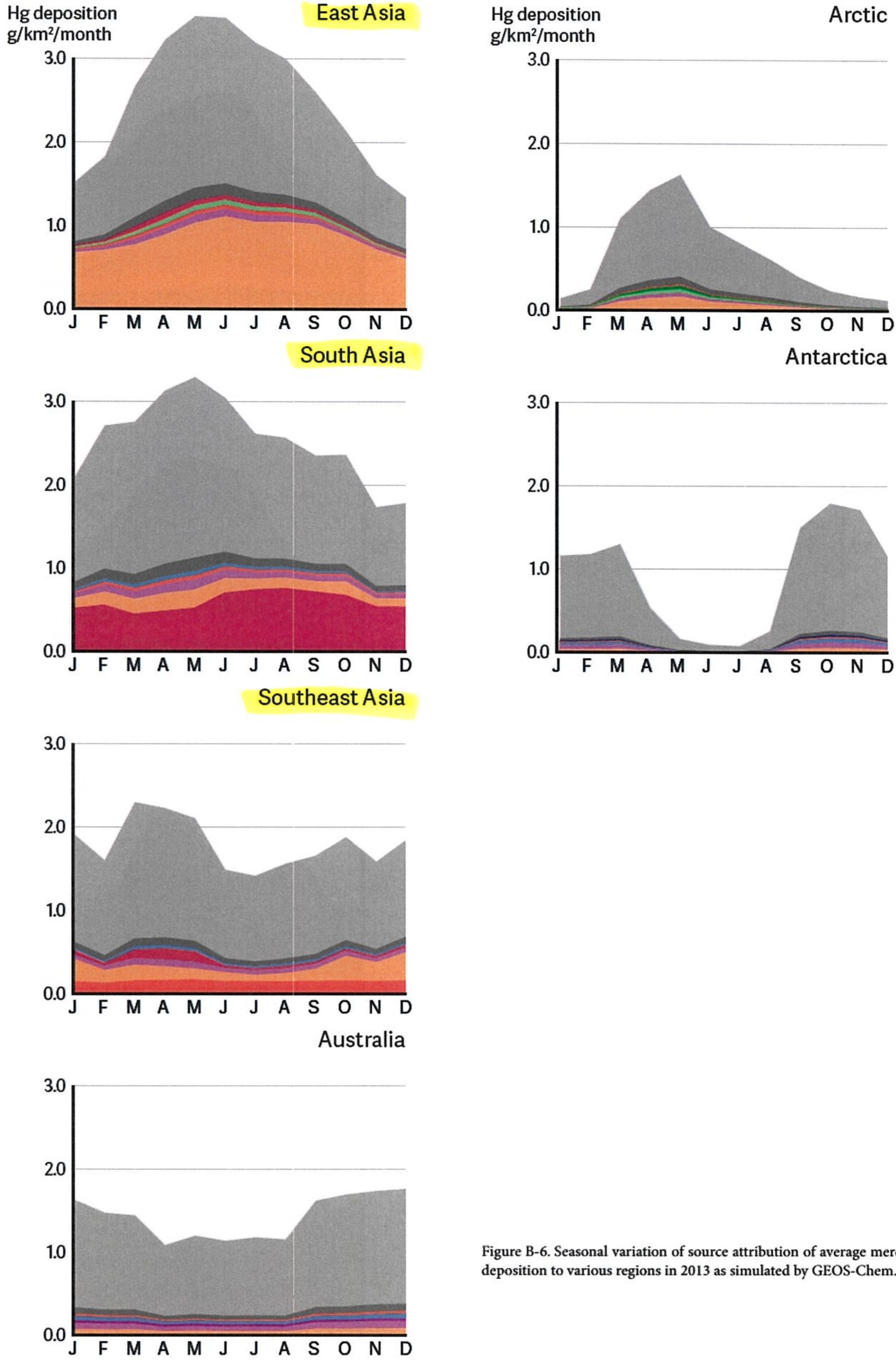
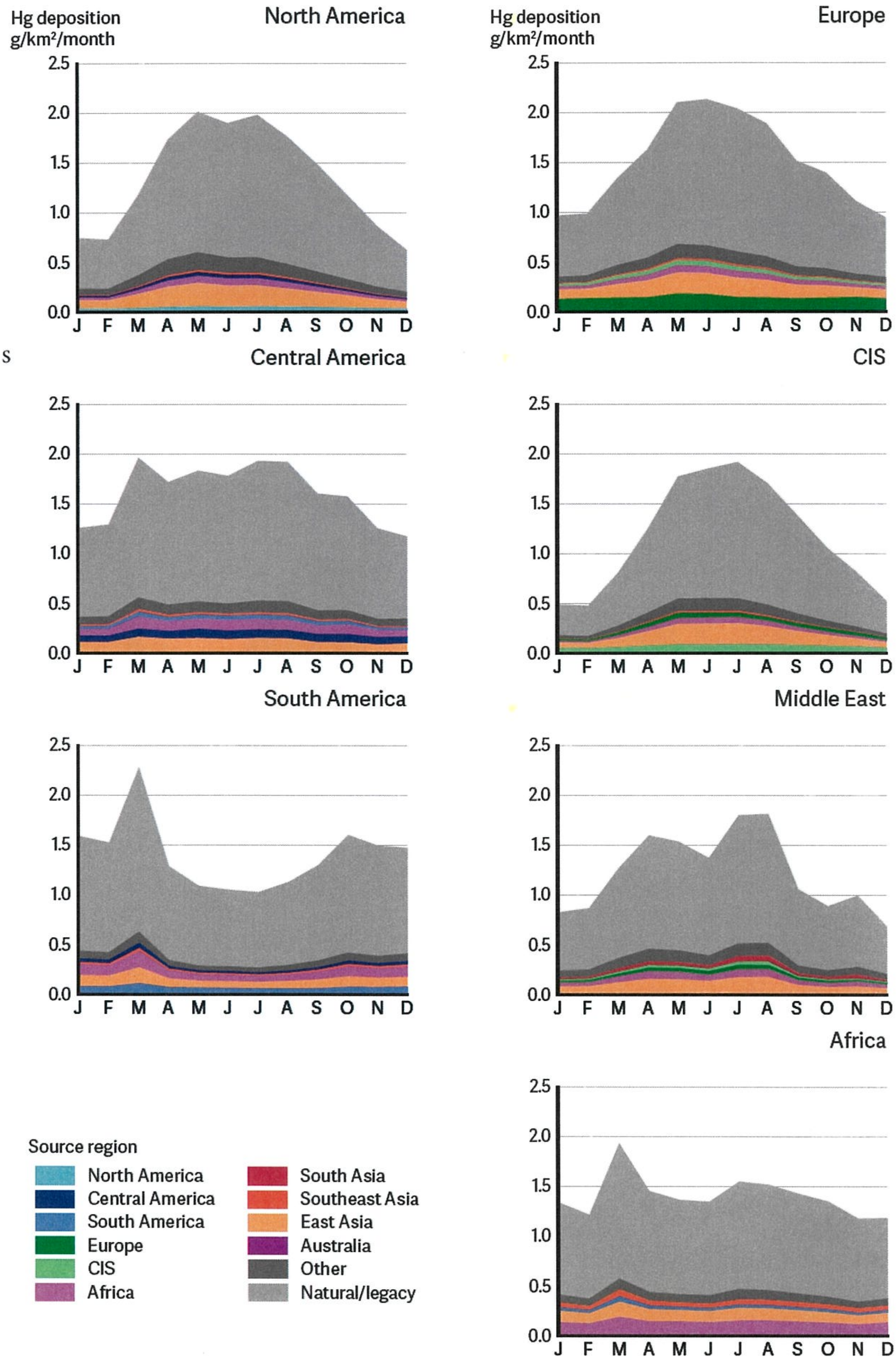


Figure B-6. Seasonal variation of source attribution of average mercury deposition to various regions in 2013 as simulated by GEOS-Chem.


Hg deposition g/km²/month
North America
Europe
Central America
CIS
South America
Middle East
Africa
2.5
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
Source region
North America
Central America
South America
Europe
CIS
Africa
South Asia
Southeast Asia
East Asia
Australia
Other
Natural/legacy

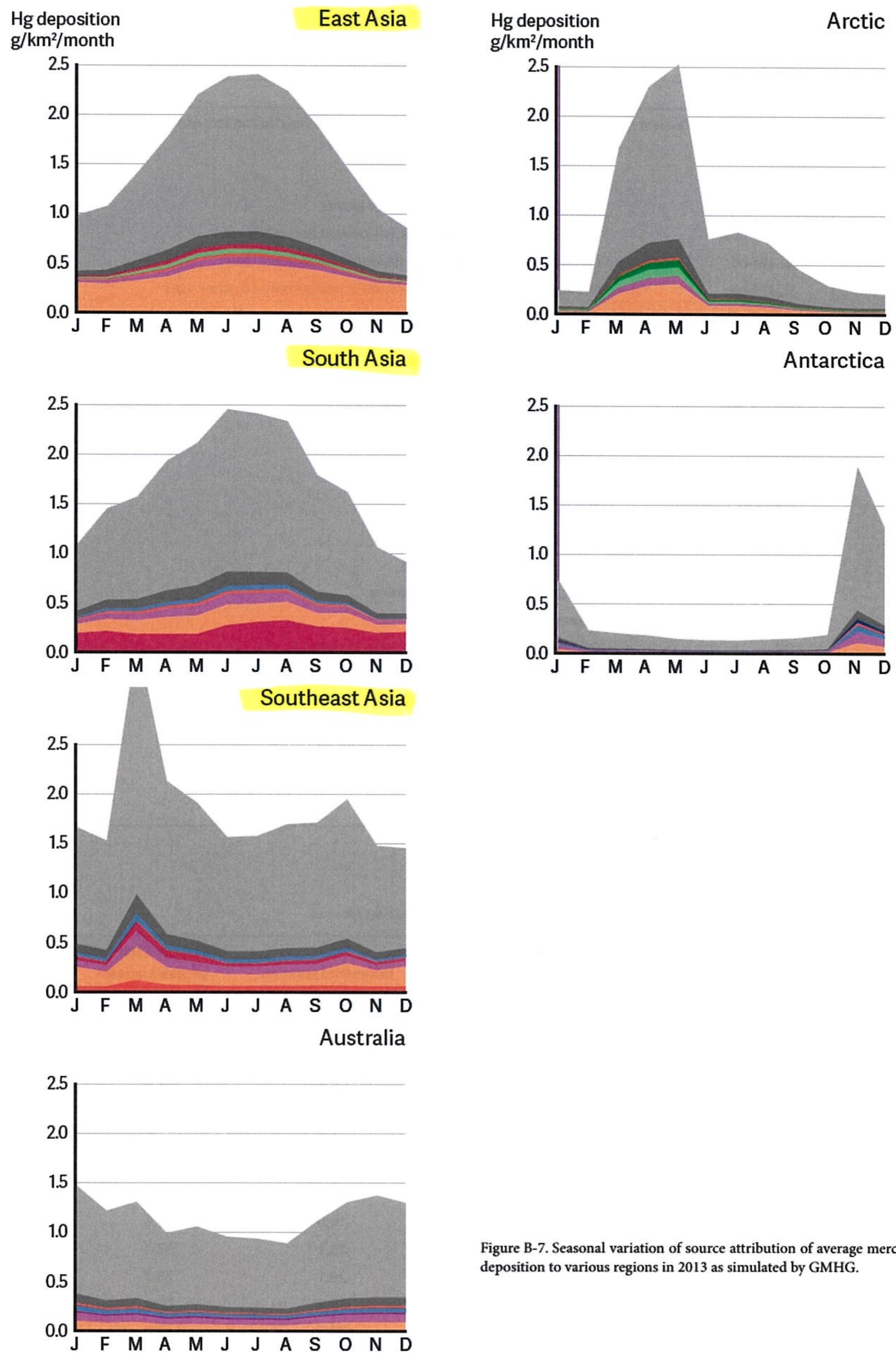


Figure B-7. Seasonal variation of source attribution of average mercury deposition to various regions in 2013 as simulated by GMHG.

B.3. Mercury deposition from different emission sectors

Table B-5. Definition of groups of emission sectors

Sector code	Description
Stationary combustion sources (power plants and distributed heating and energy uses excluding industrial uses)	
SC-PP-coal	Coal combustion in power plants
SC-PP-oil	Oil combustion in power plants
SC-PP-gas	Natural gas combustion in power plants
SC-DR-coal	Coal combustion in domestic residential and other uses
SC-DR-oil	Oil combustion in domestic residential and other uses
SC-DR-gas	Natural gas combustion in domestic residential and other uses
Industrial sources (including stationary combustion for industry)	
SC-IND-coal	Coal combustion in industry
SC-IND-oil	Oil combustion in industry
SC-IND-gas	Natural gas combustion in industry
PISP	Pig iron and primary steel production
NFMP-Cu	Copper primary production
NFMP-Pb	Lead primary production
NFMP-Zn	Zinc primary production
NFMP-Al	Aluminium primary production
NFMP-Au	Large-scale gold production
NFMP-Hg	Mercury production from mining
CEM	Cement production
OR	Oil refining
Intentional use and product waste associated sectors	
ASGM	Artisanal and small-scale gold mining
CSP	Chlor-alkali industry
WI	Incineration of product waste in large incinerators
WASOTH	Other disposal of product waste
CREM	Cremation emissions

Table B-6. Deposition from different emission sectors as simulated by GLEMOS, tonnes/year

	Area, km²	Stationary combustion sources	Industrial sources	Intentional use and product waste
NAM	1.69×10^7	24.1	20.0	25.0
EUR	5.53×10^6	22.8	12.6	12.7
SAS	5.07×10^6	29.3	18.7	14.2
EAS	1.16×10^7	52.0	54.2	21.9
SEA	4.94×10^6	6.9	13.4	14.0
PAN	8.06×10^6	3.5	8.5	11.2
AFR	3.00×10^7	28.0	39.8	57.4
MDE	5.17×10^6	2.6	6.3	7.4
MCA	5.21×10^6	4.0	10.8	15.6
SAM	1.53×10^7	7.3	25.1	37.4
CIS	1.79×10^7	19.6	29.1	28.0
ARC	2.24×10^7	8.2	19.7	22.6
ANT	3.42×10^7	9.1	23.3	40.3

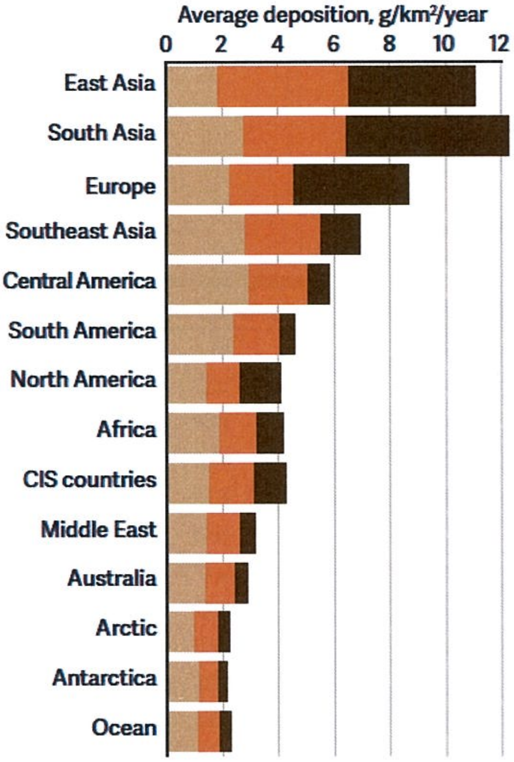
Table B-7. Deposition from different emission sectors as simulated by GEOS-Chem, tonnes/year

	Area, km²	Stationary combustion sources	Industrial sources	Intentional use and product waste
NAM	1.69×10^{7}	32.4	34.8	41.1
EUR	5.53×10^{6}	22.3	15.6	15.3
SAS	5.07×10^{6}	27.7	21.2	17.9
EAS	1.16×10^{7}	56.9	71.6	42.0
SEA	4.94×10^{6}	7.9	14.1	16.4
PAN	8.06×10^{6}	4.7	11.1	16.4
AFR	3.00×10^{7}	33.7	50.0	80.7
MDE	5.17×10^{6}	3.7	8.3	10.2
MCA	5.21×10^{6}	5.2	13.2	22.3
SAM	1.53×10^{7}	11.3	34.1	58.6
CIS	1.79×10^{7}	27.3	42.9	40.4
ARC	2.24×10^{7}	9.0	19.8	20.3
ANT	3.42×10^{7}	8.0	19.1	34.2

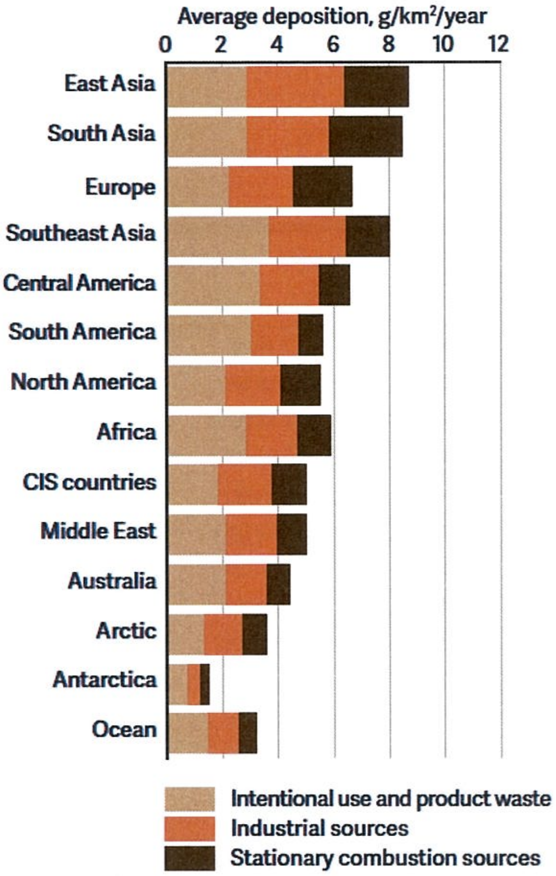
Table B-8. Deposition from different emission sectors as simulated by GMHG, tonnes/year

		Stationary combustion sources	Industrial sources	Intentional use and product waste
NAM	1.69×10^{7}	22.9	33.9	36.4
EUR	5.53×10^{6}	11.4	12.8	12.7
SAS	5.07×10^{6}	13.0	15.0	14.8
EAS	1.16×10^{7}	26.2	40.3	34.0
SEA	4.94×10^{6}	7.4	13.6	18.4
PAN	8.06×10^{6}	6.3	11.8	17.4
AFR	3.00×10^{7}	34.4	55.5	86.9
MDE	5.17×10^{6}	5.4	9.5	11.1
MCA	5.21×10^{6}	5.7	10.9	17.7
SAM	1.53×10^{7}	13.0	26.0	47.0
CIS	1.79×10^{7}	21.4	35.1	33.6
ARC	2.24×10^{7}	17.6	31.5	30.6
ANT	3.42×10^{7}	9.2	16.3	26.3

a) GLEMOS



c) GMHG



b) GEOS-Chem

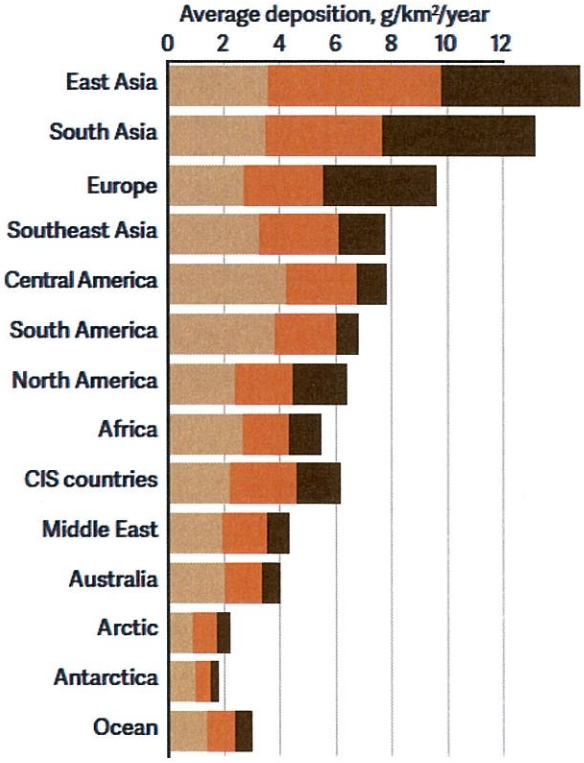


Figure B-8. Contribution of emissions from the three sector-specific groups to average mercury deposition from contemporary anthropogenic sources over various geographical regions in 2013.

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Abstract Volume

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1g: Mercury through time – Reconstructing Hg-deposition using natural archives

MO-001

FIRST MILLENIAL RECORD OF ATMOSPHERIC GASEOUS HG

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Environmental regulations on mercury (Hg) emissions and associated ecosystem restoration are closely linked to what Hg levels we consider natural. It is widely accepted that atmospheric Hg deposition has increased by a factor 3 ± 1 since pre-industrial times. However, no long-term historical records of actual atmospheric gaseous elemental Hg (GEM) concentrations exist. In this study we report Hg stable isotope signatures in two Pyrenean peat records (southwestern Europe) that are used as tracers of Hg deposition pathway (Δ200Hg, wet vs dry Hg deposition) and atmospheric Hg sources and cycling (δ202Hg, Δ199Hg). Three cores from the Pinet peat bog (880m asl) were used to reconstruct Hg deposition for the past 10,000 years. A comparison with Estibere (2100m asl) peat record reveals both similarities and differences in terms of Hg deposition. By anchoring peat-derived GEM dry deposition to modern atmospheric GEM levels we are able to reconstruct the first millennial-scale atmospheric GEM concentration record, which is in good agreement with post-1970 monitoring data and a reconstruction based on polar firn air from 1940 to 2005. Historical variations in peat Hg stable isotope signatures reveal different periods of anthropogenic influence over the past millenniums. We suggest that deforestation and associated biomass burning Hg emissions caused a first shift in δ202Hg during the medieval and Renaissance periods. The maximum GEM concentration found during the 20th Century and exceeds by a factor of 15 the natural Holocene background. Our findings suggest therefore that Human impacts on the global mercury cycle are subtler and substantially larger than currently thought.

MO-002

USING TREE-RINGS TO RECONSTRUCT MERCURY EMISSIONS ASSOCIATED WITH GOLD MINING IN THE KLONDIKE (YUKON TERRITORY)

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Atmospherically mobile Hg(0) can be converted, post-deposition, to toxic methylmercury in terrestrial and aquatic environments posing significant risks to human and ecosystem health in regions far from emission sources. Accurate projections of future Hg exposure and impacts will partly depend on our ability to understand changes in the atmospheric Hg pool, but long-term knowledge of atmospheric Hg variability is limited to ~2 decades of instrumental monitoring. Natural Hg archives such as ice cores, tree-rings and lake sediments have the potential to fill this knowledge gap. Tree-rings are ideal since they are annually resolved, span multiple centuries, and cover large areas of Earth's surface. Few studies concerning a small number of species have shown the potential of tree-rings to record local Hg emissions, but additional proof-of-concept is needed. We present an annually resolved tree-ring Hg record from a stand of white spruce ~100 m from the Bear Creek Gold Room site, Klondike Goldfields, where the Au-Hg amalgam method was used to recover fine gold from placer ore. Bear Creek operations began in 1905, but were greatly expanded in 1930 when most Klondike recovery operations were consolidated to the Bear Creek site. Results from 15 trees reveal a common pattern in tree-ring Hg over the last ~150 years (mean $r = 0.60$, $p<0.01$), extending into the pre-mining era. The lowest Hg concentrations occur prior to the Klondike Gold Rush (1896-1899). Initial Bear Creek operations mark a rise in tree-ring Hg concentrations, but this signal is small compared to a major step to peak values in the 1930s coinciding with consolidated operations. Tree-ring Hg declines rapidly after the cessation of Bear Creek operations in ca. 1966. This result suggests the principle Hg intake pathway is likely air-leaf assimilation rather than root uptake from contaminated soil, as there is no delayed decline in tree-ring Hg after the cessation of Bear Creek operations, despite a legacy of elevated soil Hg concentrations to this day. Finally, we observe that post-1966 Hg concentrations are slightly higher than pre-industrial values, likely reflecting higher global atmospheric Hg(0) concentrations. This is the first study of white spruce tree-ring Hg, and only the second to measure this variable at annual resolution. These results demonstrate that this species is a reliable recorder of local emissions, and offers great promise for longer-term reconstructions of atmospheric Hg at potentially broader spatial scales.

MO-003

LATE CRETACEOUS VOLCANISM AND ASSOCIATED CLIMATE CHANGE INFERRED FROM ELEVATED THG IN MARINE INVERTEBRATE FOSSILS

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Large-scale, semi-continuous volcanism in India produced the Deccan Traps and is coincident with the Chicxulub impactor and extensive end-Cretaceous extinction, including the demise of dinosaurs. Linking the timing of volcanism and impact events with local records of climate change and extinction has proven difficult with existing methods. We present total mercury concentrations (THg) derived from the biogenic carbonate of marine mollusks at intervals spanning before,

during, and after the period of active Deccan volcanism. THg values were determined by cold vapor atomic fluorescence spectroscopy after digesting sample carbonate material in 4N HNO3 at 70°C. The same shells were measured for their clumped isotopic composition (Ca13C18O16O2 abundance), an isotopic quantity directly related to the water temperature where the bivalves lived. We document a pattern of increased temperatures co-occurring with THg anomalies of 10 to 43 ng/g relative to a background of 0.5 to 4 ng/g in shells from numerous localities proximal to and distal from the proposed volcanic source. The beginning of the warm interval (~100 to 250 ka prior to the end Cretaceous boundary) coincides with the onset of Deccan Traps volcanism. At one locality, with the highest temporal sample resolution (Seymour Island, Antarctica), we find evidence for multiple THg anomalies (~10 to 17 ng/g), potentially corresponding to separate phases of Deccan Traps activity. Taken together, measuring paleotemperature and THg in the same material allows for direct comparison between indicators of volcanism and records of climate change. These data strongly suggest volcanic forcing caused end-Cretaceous climate change, and shed new light on concurrent extinction patterns. The combined THg and paleotemperature records also provide new insight into long-standing questions regarding the role of volcanism as opposed to bolide impact on observed extinction patterns at the end of the Cretaceous. This method could similarly be applied to other past volcanic events to further constrain links between climate change and volcanism through Earth history.

MO-004

TESTING THE EFFECT OF AIR HG EXPOSURES ON FOLIAGE AND TREE RING CONCENTRATIONS AT 3 LOCATIONS

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Concentrations of atmospheric mercury (Hg) in the past are not known. As part of a larger project, our team is investigating whether tree rings are reliable archives of changing atmospheric Hg concentrations over time on local, regional, and/or global scales. In general it is thought that trees take up gaseous elemental mercury (GEM) through their foliage (via the stomatal openings and through the cuticle). Gaseous oxidized mercury (GOM) is not thought to be taken up by the foliage. Additionally, the effect of different atmospheric GOM composition ontree ring Hg is uncertain. We tested the hypothesis that Hg concentrations of tree growth rings and needles of coniferous tree species would be influenced by air chemistry, Hg concentration, and field conditions at different locations. To do this, 5-6 year old Austrian pines (Pinus nigra) purchased from a farm in rural Oregon, USA, were moved in 25 gallon pots in their original soil to 3 locations: an urbanized site in Reno, Nevada (approximately 1370 m), experiencing proximate effects of petroleum-based combustion along a busy interstate; a mountaintop site at Peavine Peak (approximately 2518 m), 12 km west of Reno, influenced by the free troposphere; and an oceanside site at the UCSC Arboretum, Santa Cruz California (approximately 140 m), interacting directly with maritime fog thought to carry relatively high concentrations of methylmercury. Each location has been identified as having different compounds of GOM (HgCl2, HgBr2, Hg-nitrogen and sulfur compounds, Hg-organic compounds). Needle data collected from the first year (n=5 trees from each site) showed significant increases at all sites relative to those from trees as originally received. Highest concentrations were measured at the coastal location ($p<0.05$). We also tested for whorl age and effect of tree orientation at the mountaintop and urban location on Hg concentration in foliage. After a year there was no influence of whorl age or orientation on needle concentration. The wood of the trees showed an increase in Hg in the most recent year of growth at 2 locations (Peavine Peak and Santa Cruz) and no increase at the urban Reno location. Tree orientation does not appear to be a factor in the radial distribution of Hg within the annual growth rings for any location.

MO-005

RECONSTRUCTING CURRENT AND HISTORICAL HG DEPOSITION FROM A BELUKHA ICE CORE: ARE REGIONAL OR GLOBAL CHANGES OF MERCURY EMISSIONS RECORDED?

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High mountain intercontinental glaciers are very suitable natural archives to reconstruct current and historical Hg deposition reflecting changes of atmospheric Hg concentrations both on the global and regional scale. Belukha glacier in the Siberian Altai provided a 300 years high-resolution record of Hg concentrations allowing to consider not only the long-term trend (based on an average of 5-10 year period values), but also the dynamics of current changes (1-2 years), as well as to fix the short-term events, both natural and anthropogenic. Hg concentrations in ice core range from < 0,04 to 3,87 and from 0,07 to 8,89 ng/L for Hg reactive and Hg total, respectively, and reflect seasonal, intra- and inter-annual variations and long-term trend of concentrations in the period 1700-2001. Large variability of Hg concentrations is observed partly due high resolution and seasonality. Short-term Hg changes in ice-core mostly related to dust or volcanic input, while long-term changes of Hg levels in the Altai are mainly determined by global Hg sources. Although the Hg concentration in the ice core from 1740 to 1850 apparently increased also due to the contribution of the regional component, i.e. mining and metallurgical industry of Rudny

Altai, as evidenced by correlation between Hg concentrations and volumes of ore smelting and silver production. Since 1850 regional contribution decreased and the global one increased, and after 1880 mercury concentrations in ice core reflected in a greater extent the global atmospheric mercury changes. The most significant increasing of Hg concentrations observed from 1940 with maximum in 1970th and decline during the 1980s that is in agreement with general trends of other environmental archives. Concentration levels are in the same order of magnitude as values from firn and ice cores of the Tibetan Plateau, Canada, Canadian Arctic, and Greenland. High Hg concentrations at the end of the 20th century founded in Belukha ice core can be explained by rising emissions from coal combustion in Asia. Hg concentrations in ice core change synchronously with modelled global atmospheric mercury emissions over the past 150 years. Average THg fluxes in Belukha ice core changed from 0,30 (preindustrial) to 0,84 (industrial) µg/m2y, hence atmospheric Hg deposition in industrial time has been enriched by a factor of 2.8.

MO-006

INFLUENCE OF WILDFIRES ON MERCURY LOADING TO NORTHERN LAKES AND PEATLANDS

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Heavy metals previously accumulated in soils and biomass can be remobilized by wildfires and deposited in aquatic environments by atmospheric transport or subsequent catchment erosion. Because wildfire frequency and intensity are predicted to increase in northwestern Canada in response to climate change, understanding the impact of wildfires on freshwater ecosystems is important to better plan for and manage the potential consequences of climate change. Increasing concentrations of mercury have recently been reported in fishes in the Northwest Territories (Canada) and this rise could be attributed to increased atmospheric mercury deposition from long-range sources, changes in bioavailability of mercury from climate warming or remobilisation of previously deposited mercury. We explore the hypothesis that forest fires are a significant source of mercury to Northwest Territory lakes using a paleoenvironmental approach. We reconstructed mercury deposition history and forest fire history in 3 dated lake sediments cores and 2 dated peatland cores from the Great Slave Lake region in the southern Northwest Territories. Radioisotope dating methods (210Pb and 14C) were used in combination to build an age-depth model for each core. Wildfire history was inferred through macroscopic charcoal analysis and trace mercury concentrations in the sediments and peat were measured in laboratory. Time series analysis will be used to determine the potential contribution of wildfire to mercury deposition. Whereas ombrotrophic peatlands solely record the influence of atmospheric depositions, lake sediments also record the effect of increased catchment erosion that usually follows a wildfire. Therefore, these complementary records of deposition (lake and ombrotrophic peatland) will be used in a single analysis to distinguish the relative influence of different mercury transportation pathways to aquatic ecosystems through time.

MO-007

HIGH-RESOLUTION CHRONOLOGY OF MERCURY AND ITS ASSOCIATION WITH POLYCYCLIC AROMATIC HYDROCARBONS AND LEAD IN A VARVED ESTUARINE SEDIMENT CORE

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Contemporary and historical information obtained from examination of natural archives has been critically important to the assessment and understanding of the biogeochemical cycling of Hg and influence of human activities. Few archival studies of Hg, however, include other geochemical indices that can aid and constrain the interpretation. Here we present a high-resolution chronology of Hg accumulation between 1727 and 1996 as determined in a well-studied sediment core from the Pettaquamscutt River Estuary in Rhode Island, northeast U.S. The Hg accumulation in this scrupulously dated, varved repository (1-3 y resolution) provides a quantitative means for assessing the magnitude, timing, and relative source strengths of human-related Hg emissions and deposition over three centuries. The significance of these findings is examined relative to (1) other temporal reconstructions of Hg deposition in urban, regional, and remote settings, and (2) historical depositional patterns of pyrogenic polycyclic aromatic hydrocarbons (PAHs), lead (Pb) and its isotopes (206Pb/207Pb) that have been determined in the same core.Broadly, Hg deposition in Pettaquamscutt sediment parallels the temporal patterns of PAHs, which track growth in industrialization and decentralized regional coal use between 1850 and 1950, as well as increased use of petroleum after 1950. There is little suggestion of a North American Hg signal predicted to be associated with extensive silver and gold mining in the western U.S. between 1850 and 1900 suggesting such releases have been slow to participate in global cycling. A broad maximum in sedimentary Hg accumulation is evident during the 1926-1990 time period. The largest flux ratios for Hg, which occurred during 1949-1976, are consistent with the predicted influence of additional sources and commercial products. In contrast, the temporal patterns for the sedimentary accumulation of Hg reported for remote lakes show a gradually increasing trend from about 1850 to modern times. The question of whether Hg accumulating in the estuary is derived primarily from either local or more regional sources is explored given the importance of atmospheric deposition in the environmental cycling of PAHs, Hg, and Pb.

MO-008

ANTHROPOGENIC MERCURY DEPOSITION IN FLIN FLON MANITOBA AND THE EXPERIMENTAL LAKES AREA ONTARIO (CANADA): A MULTI-LAKE SEDIMENT CORE RECONSTRUCTION

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High-resolution records of anthropogenic mercury (Hg) deposition were constructed from dated sediment cores from nine lakes located 5-75 km from the Flin Flon, Manitoba Cu-Zn smelter (formerly one of North America's largest atmospheric Hg point sources) and five lakes in Experimental Lakes Area (ELA), Ontario; a region remote from Hg point sources. For the Flin Flon lake records we have taken a novel approach integrating the relation between Hg inventories (minus that contributed from long-range transport [i.e. that observed at the ELA] and the residual normalized for prevailing wind direction) and distance from the smelter to scale up the measurements to get a landscape scale picture of Hg deposition over time. To our knowledge this is the first time such a quantitative spatial-temporal reconstruction of contaminant deposition and inventory with respect to a point source has been performed. The sediment records of anthropogenic Hg flux and inventory were remarkably consistent among the ELA lakes and are also in good quantitative agreement with monitoring data (post-1992) supporting the veracity of our record. The anthropogenic Hg flux to the ELA was 0.6 µg m-2 year-1 in the late 1800s increasing to 2.0 circa 1900 rising steadily till late-1930s thereafter rising sharply and peaking in the early-1950s at 6.1, followed by a slight decline in the 1960s and 70s (5.3 µg m-2 year-1). A trend similar to long-term Hg emissions estimates for the Great Lakes region over the last century. That is until sediment recorded anthropogenic Hg deposition began rising post-1990, reaching a maximum of 6.5 µg m-2 year-1 in the most recent time interval (2005-2010), suggesting that increasing Hg emission from very distant sources is offsetting reductions of Hg emissions in the Great Lakes region and North America. In contrast to the ELA, the anthropogenic Hg deposition and inventories of the Flin Flon region lakes varied by 2 orders of magnitude. The relation between Hg inventories and distance from the smelter was used to estimate the total smelter sourced Hg fallout within a 50-km radius (64 tonnes) and in five-year time-steps for the same. The propensity for Hg to undergo long-range, even global transport explains why Hg deposition within 50 km was ~11% of estimated releases. That is until smelter releases were reduced >10-fold (post-2000), after which observed deposition equaled or exceeded smelter releases, suggesting landscape re-emission /remobilization of legacy Hg is a major ongoing regional source of Hg.

2c-1: Sources and cycling of mercury in terrestrial ecosystems

MO-009

THE ROLE OF THE AMAZON RAINFOREST IN REMOVING ATMOSPHERIC MERCURY

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Atmospheric mercury is effectively trapped in forest canopies by deposition on leaves surface. Mercury compounds that accumulate on foliage are then transferred to the soil through litterfall and its decomposition, and via throughfall. The Amazon rainforest covers approximately 5.5 million km2, representing over half of the planet's remaining rainforests. Nevertheless, the role of the Amazon in the balance between Hg emissions and depositions is still a field of research with high uncertainties evolved. The aim of this work was to quantify the amount of Hg removed from the atmosphere and stocked in this forest every year. The impact of deforestation on the deposition/emission mass balance is also discussed.

Total Hg deposition was calculated as the sum of Hg deposited by litterfall (HgLitterfall) and by throughfall (HgThroughfall). Calculations were performed based on a large set of data obtained from the literature. The removing rate of atmospheric Hg would be of 121 g km-2 y-1, with 49 g km-2 y-1 due to HgLitterfall. Dry deposition was also estimated to 103 g km-2 y-1. Combining this data with the Amazon rainforest area (5,475,737 km2), results in a total rate of mercury immobilization of ~662 ton y-1. In a global scale, the total atmospheric Hg deposition to land has been estimated to 3,200 ton y-1. The Amazonian rainforest would therefore be responsible for the immobilization of, at least, ~21% of the total atmospheric Hg deposited to land. This high efficiency to remove atmospheric Hg can be related to many parameters, such as: large forest area, high wet deposition, high leaf area index and high leaf lifetime (both increasing Hg concentration in foliage/litter) and high litterfall rate.

On the other hand, the Amazonian forest suffers constant deforestation, which is mainly conducted by forest burning. This process results in Hg volatilization stocked in vegetation and superficial soil; we also showed that it also significantly enhances soil Hg emissions in deforested area. Considering the annual rate of deforestation of the Brazilian Amazonian forest (11,075 ± 7,177 km2 y-1 for the 2004-2014 period) we estimated that ~6 ton Hg can be reemitted to the atmosphere each year due to deforestation. One aspect that has never been included in this mass balance is that deforestation also results in a loss of the forest capacity to remove atmospheric Hg. When considering the deforestation area for the 10 last years and the dry deposition rate, we estimated that the removing loss was ~97 ton Hg.

MO-010

EXCHANGE PROCESSES OF GASEOUS MERCURY WITH THE CLOSED ECOLOGICAL SYSTEM OF THE MASOALA RAINFOREST, ZOO ZURICH

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The nature and relative importance of exchange processes of elemental mercury (GEM)) between the terrestrial ecosystem and the atmosphere is still subject to debate in the research comunity. Even on the question, whether the global terrestrial ecosystem serves as a net sink or source to the atmosphere, one has not yet agreed upon. Thereby the uncertainty regarding the leaf-atmosphere exchange of GEM plays a pivotal point. Two measurement techniques have primarily been used to study GEM fluxes: dynamic flux chambers and micro-meteorological measurements. While both methods have their benefits, their shortcomings introduce substantial uncertainties. A novel approach has been used in this study to overcome some of the deficiencies. As a study site, we used the closed ecological system of the Masoala Rainforest, Zoo Zurich, a project within the framework of the zoo's conservation strategy. On an area of 10'856 m² a dense plantation reproduces a piece of Madagascan rainforest. A hall constructed from transparent ethylene tetrafluoroethylene foil provides a tropical climate, which is regulated by a ventilation system. This setup, resembling a scaled-up flux chamber, presents a unique opportunity to study the exchange processes of a terrestrial ecosystem with the atmosphere. Gaseous elemental mercury was therefore measured in the ventilation system of the Masoala Rainforest. Depending on the ventilation regime different situations could be studied. Generally, we observed GEM concentrations inside the Masoala hall to be lower by about 30% compared to outdoor air. During periods where the air was merely recirculating inside the hall (i.e. with no influx of fresh outdoor air), GEM levels indoors steadily declined, indicating that the Masoala hall is a net sink for GEM. The analysis of our time series allowed the derivation of an uptake rate of mercury within this rainforest ecosystem. Ongoing work includes the analysis of plant material, soil, and water from the Masoala Rainforest. We believe our work can provide a new approach to assess mercury fluxes between terrestrial ecosystems and the overlying atmosphere. With our study, we contribute to the existing knowledge gap regarding mercury exchange fluxes and help to improve the global mercury mass balance.

MO-011

MERCURY EMISSION TO THE ATMOSPHERE DOMINATES ANNUAL MASS BALANCE OF A BOREAL PEATLAND: TIME TO RETHINK TIMELINES FOR RECOVERY?

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To estimate the potential of different ecosystems as sinks or sources for atmospheric Hg, reliable quantification of land-atmosphere exchange of gaseous elemental Hg (GEM) is crucial. We have made the first annual Hg budget based on continuous measurements of peat-atmosphere exchange of GEM using a novel relaxed eddy accumulation (REA) system. The annual Hg mass balance was dominated by net GEM emission (10.2 µg m-2) due to substantial evasion between May and October. The annual wet bulk deposition of Hg was 3.9 µg m-2. The annual discharge export of Hg from the peatland area (1.9 km2) amounted to 1.3 µg m-2. The GEM evasion rate, a factor of 2.6 higher than wet bulk deposition, can be explained by the recent reduction in the atmospheric Hg concentration to a value below the compensation point for this peatland, turning it from a sink into a source of Hg emission back to the atmosphere after decades of Hg accumulation. This is consistent with the Hg concentration gradients in the superficial peat which decline from a Hg concentration peak at about 30 cm depth (110 ng g-1, corresponding to Hg emission peaks during the 1950s) towards the surface (24 ng g-1). Under the assumptions that environmental conditions remain stable and that catchment runoff is dominated by Hg from the uppermost peat layers, it will take around 80 years to deplete the entire pool of legacy Hg in the uppermost 34 cm to a background concentration level of 20 ng THg g-1. We suggest that the strong Hg evasion demonstrated in this study means that open boreal peatlands and thus downstream ecosystems may recover more rapidly from past atmospheric Hg deposition than previously assumed.

Given the current international efforts to protect human health and the environment from the adverse effects of mercury in accordance with the United Nation's 2013 Minamata Convention on Mercury, we believe our findings contribute to a better understanding of how emission reductions will influence mercury cycling in northern peatlands and their role for the mercury status of fresh water fish in the Northern Hemisphere. Our findings also raise the question as to whether recent reductions of atmospheric mercury concentrations have led to net evasion from other ecosystems as well, such as forests and oceans. We believe that the REA technique could be applied more widely to define the balance between new emissions and re-emission for different ecosystems.

MO-012

EFFECT OF PH AND DOC ON PARTITIONING OF MERCURY ON MINERAL FORESTED SOIL SURFACE

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Acid deposition has acidified northeastern forest ecosystems. Regulation of emissions and subsequent decreases in acid deposition are reversing acidification. However, recent studies indicate that concentrations of dissolved organic carbon (DOC) have increased, apparently in response to decreases in acid deposition and/or changing climate. This study was conducted to evaluate how changes in acidity and concentrations of DOC can affect soil adsorption/desorption of mercury (Hg). We initiated a series of adsorption experiments using soil collected from mineral horizon at Honnedaga Lake-watershed a forested site in the Adirondack region, NY. The DOC stock solution for this experiment was obtained by soaking freeze-dried Oa horizon in deionized water for 3 days and the suspension was filtered and stored at 4C. We equilibrated 50 ml of either 0, 3.5, 8.1, 25.2, 41.9 and 56.4 mg/l solutions of DOC with 1 g of sieved, freeze-dry mineral soil on a shaker for 24 hr. Either nitric acid or sodium hydroxide was added to the initial experimental solutions to adjust pH. Particulate matter was removed from the final solutions by centrifugation and filtration. The supernatant was measured for Hg and DOC concentration and pH. The results of the adsorption experiment demonstrated that changes in solution pH have a large effect on Hg and DOC release from forest mineral soil. Note the mass of total Hg in soil was much greater than the mass of initial Hg in solution (approximately 230 ng on soil vs 0 to 1.3 ng in solution in each trial tube), therefore we were not able to accurately evaluate the adsorption behavior of Hg, rather desorption behavior of soil was examined. In the pH range 4-4.5, there was adsorption of Hg and minimal desorption of DOC, but as the pH increased above 4.5 there was a gradual increase in desorption in both DOC and Hg. Hg in solution reached a maximum percentage of soil Hg of approximately 2% at pH 5.9. A strong correlation was observed between desorbed DOC and Hg over the pH range of our experiment ($R2 = 0.91$) which suggests that functional groups of dissolved organic matter strongly complex Hg. Consequently Hg desorption is driven by the release of dissolved organic matter from soil. Results of this experiment can be applied in characterization of a complexation model of Hg, organic compound, and soil surface.

MO-013

QUANTIFYING MERCURY IN LEAVES, BARK AND WOOD OF EIGHT TREE SPECIES ACROSS FOUR NORTHEASTERN FORESTS USING APPROPRIATE METHODS FOR SAMPLE PREPARATION AND ANALYSIS

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Mercury deposition affects remote areas such as forests, but the amount of Hg in trees is not well known, in part because concentrations of Hg in wood are below detection limits of some methods. For example, ICP-OES requires a liquid sample, which in the case of wood, might be 1/100th of the concentration of the tissue sample prior to digestion and dilution. Solid samples can be directly analyzed by thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry through a Total Mercury Analyzer, giving much lower detection limits, but questions remain about sample preparation, such as whether air-dried samples would be suitable for analysis. We examined the effects of drying temperature during sample preparation using wood samples at the Hubbard Brook Experimental Forest, New Hampshire, USA. Samples that were freeze-dried or oven-dried at 65 ˚C were suitable for analysis of Hg, whereas oven-drying at 103 ˚C resulted in Hg losses, and air-drying resulted in Hg gains, presumably due to sorption from the indoor atmosphere. Having established suitable methods, we analyzed Hg in wood, bark, and foliage of eight tree species across four sites (Huntington Forest, NY; Sleepers River, VT; Hubbard Brook, NH; Bear Brook, ME) in the northeastern USA to determine the importance of Hg in trees. Foliar concentrations of Hg averaged 16.3 ng g-1 among the hardwood species, namely American beech (Fagus grandifolia Ehrh.), white ash (Fraxinus americana L.), yellow birch (Betula alleghaniensis Britt.), sugar maple (Acer saccharum Marshall.), and red maple (Acer rubrum L.). Foliage of conifers, namely red spruce (Picea rubens Sarg.), balsam fir (Abies balsamea (L.) Mill.) and white pine (Pinus strobus L.) averaged 28.6 ng Hg g-1), significantly higher than the hardwoods ($p < 0.001$). Similarly, bark concentrations of Hg were lower ($p < 0.001$) in hardwoods (7.7 ng g-1) than conifers (22.5 ng g-1). Species also differed significantly in Hg concentration of foliage ($p = 0.02$) and bark ($p < 0.001$). For wood, concentrations of Hg were highest in yellow birch (2.5 ng g-1) compared with all the other species (mean of 1.4 ng g-1) ($p < 0.0001$). Sites differed significantly in Hg concentrations of foliage and bark ($p = 0.02$) but not wood ($p = 0.60$). The Hg content of trees, estimated from modeled biomass and measured concentrations at each site, was higher in wood than foliage. Wood is important to Hg budgets in spite of low concentrations, because of its large mass.

MO-014

LANDSCAPE INFLUENCES ON MERCURY CYCLING AND BIOAVAILABILITY IN VERNAL POOLS

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Vernal pools are temporary seasonal water bodies found in Northeastern forests. They are subject to mercury (Hg) contamination via throughfall, leaf litter and snowmelt, and to conditions of high organic matter and low pH which support methylation of Hg to the more toxic and bioavailable species, methylmercury (MeHg). Currently, few studies have reported Hg and MeHg in vernal pools, but levels of Hg in the forest floor and streams have been shown to vary widely with landscape characteristics such as forest type, canopy cover, and land-use over small spatial scales. A suite of 21 pools were examined for Hg and MeHg levels and bioavailability across different canopy covers, with additional temporal sampling at six of the pools. Water column dissolved MeHg concentrations ranged between 0.02 to 2.76 ng/L, and from 5 - 52% of total Hg. Concentrations of total Hg in pools were correlated to dissolved organic carbon (DOC) across sites, whereas MeHg had a temporal relationship with water temperature between snow melt and drying. While coniferous sites had lower pH, canopy type alone did not predict MeHg concentrations. Wood frog and salamander embryos from pools surrounded by deciduous forest had higher concentrations of MeHg than those from coniferous sites, suggesting forest type affects bioavailability.

MO-015

ELEVATIONAL AND SEASONAL PATTERNS IN METHYLMERCURY INPUTS AND PRODUCTION FORESTS ACROSS A MONTANE ELEVATION GRADIENT

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Mercury contamination in remote regions is generally derived from atmospheric deposition. While many studies have examined patterns in mercury deposition and processing in aquatic ecosystems, less is known about the fate of mercury in terrestrial systems and particularly in montane environments. We examined soil samples collected across an elevational gradient on Whiteface Mountain in the Adirondack Region of New York to determine spatial patterns of methylmercury concentrations across the forested montane landscape. We also investigated sources of total and methylmercury inputs (throughfall, precipitation, and litterfall), as well as mercury uptake into avian species. We found that soil methylmercury concentrations were highest in the mid-elevation coniferous zone (0.39 ± 0.58 ng/g), compared to the alpine (0.28 ± 0.36 ng/g) and deciduous zones (0.17 ± 0.19 ng/g), while the percent mercury as methylmercury in soils decreased linearly with elevation. Additionally, methylmercury concentrations and percent mercury as methylmercury were highest in the Oa layer (0.30 ± 0.30 ng/g, 0.12 ± 0.16%) compared to the Oe/Oi layer (0.18 ± 0.27 ng/g, 0.07 ± 0.10%). Finally, we found litterfall mercury inputs to exhibit relationships with soil methylmercury concentrations and percent mercury as methylmercury, with the highest concentrations found in the coniferous zone (0.052 ± 0.017 ng/g, 0.10 ± 0.018%) compared to the alpine (0.039 ± 0.014 ng/g, 0.061 ± 0.023%) and deciduous zones (0.031 ± 0.020 ng/g, 0.10 ± 0.060%). Soil methylmercury concentrations and fluxes vary seasonally and appear to be driven by internal processing of ionic Hg, as opposed to atmospheric deposition of methylmercury to the forest floor. These findings are consistent with methylmercury patterns in terrestrial bird species and suggest that future declines in mercury emissions could be important in reducing litterfall mercury inputs to terrestrial systems and thus concentrations of mercury in montane avian species.

MO-016

MERCURY CYCLING AND ISOTOPIC FRACTIONATION IN FOREST ECOSYSTEMS: A MODELING STUDY

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Mercury (Hg) is subject to long-range atmospheric transport. Forest ecosystems cover >30% of the Earths land surface and are considered as an important Hg reservoir on a global scale. Recent assessments on Hg removal through vegetative Hg uptake followed by litterfall and accumulation in soil, in addition to wet deposition, suggest that global forests are a major sink of atmospheric mercury. However, the processes driving Hg cycling in forest ecosystems have not been fully understood. Forest characteristics, meteorological conditions, and surface terrain are important drivers of Hg deposition in forested area. In the past few years, data of stable Hg isotope measurement for the air, soil, biomass, and litter samples at multiple forest sites offer new insights to Hg cycling processes in forest ecosystem. In this study, we build a hybrid mass balance and isotopic fractionation model for simulating Hg transformation, translocation and isotopic composition changes in forest ecosystems. The model parameterizes mercury exchanges between forest and atmosphere, the transformation processes of deposited Hg through litterfall on forest floor, and the isotopic massdependent and independent fractionations involved in these processes. The model results are verified with the measurements of Hg concentrations and isotopic compositions of air, biomass, litter (fresh and degraded) and soil samples, as well as air-surface (air-soil and air-foliage) exchanges of elemental Hg vapor at a subtropical evergreen forest site located in Mt. Ailao Nature Reserve in Yunnan Province, Southwest China. Based on the model results, the mass budget, cycling and the forcing of Hg isotopic compositions of at the experimental forest site will be elucidated. Implications of the modeling assessment will be discussed in terms of the role of forest ecosystems in global Hg budget and its impact on the isotopic composition of atmospheric Hg.

2f-1: Mercury methylation: microbial and geochemical constraints

MO-017

MOLECULAR COMPOSITION OF ORGANIC MATTER CONTROLS THE ACTIVITY OF MERCURY METHYLATING MICROBIAL COMMUNITIES

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It is crucial to identify factors controlling the formation of the potent neurotoxic methylmercury (MeHg). In lakes, the methylation of inorganic-Hg to MeHg is biotically mediated and occurs mainly in oxygen-deficient sediments or water columns. Organic matter (OM) interacts strongly with Hg, affecting its chemical speciation, and thus its solubility, mobility, and toxicity. In aquatic ecosystems, OM is an extremely heterogeneous mixture derived from terrigenous and planktonic sources. In this study we test whether planktonic derived OM compounds control Hg methylation rates in sediments of ten boreal lakes of different trophic status (total phosphorus, TP: 8–198 µg/L) and receiving different amounts of dissolved organic carbon inputs (DOC: 3.8–33.1 mg/L). We characterized the molecular composition of the sediment OM by a pyrolysis–gas chromatography/mass spectrometry (Py-GCMS) method. High-throughput sequencing of amplified taxonomic marker genes (16S rRNA) and genes specific for Hg methylators (hgcA) were used to characterize microbial communities. The highest Hg methylation rate constants (km) were found in lakes dominated by planktonic derived OM (km = 0.038–0.075 in 1/day, n=4). Lower values were observed in lake sediments enriched in terrigenous OM (0.0095–0.013, n=5) or in invertebrate chitin associated compounds (0.013, n=1). Bacterial production rate in sediments dominated by planktonic and chitin derived OM was significantly higher than in sediments characterized by terrigenous OM (p-value<0.001). The most abundant organisms with potential for Hg methylation were methanogens together with sulphate- and iron-reducing bacteria. Bacterial community composition and Hg methylating bacteria composition varied among lakes independently of km. In contrast, the abundance of planktonic-derived OM compounds (chlorophyll, protein, and cell wall lipids) predicted the variability in both the km and BP. We conducted additional laboratory incubation experiments to assess the relative importance of three OM sources, with differentiated molecular OM composition, on the km of two lakes with low in situ km. The substrates consisted of an algae, a cyanobacteria and a humic soil extract. The results of lake sediment amendments suggested that cyanobacterial-derived OM enhanced Hg methylation processes by boosting bacterial activity whereas algal and soil derived OM increased Hg methylation by augmenting Hg availability. Our findings provide additional mechanistic understanding of the effect of OM molecular composition in Hg methylation processes and shed light on the diversity of Hg methylating microbial communities in boreal lake sediments.

MO-018

THIOL FUNCTIONAL GROUPS OF NATURAL ORGANIC MATTER AND BACTERIA MEMBRANES AND THEIR CONTROL OF HG(II) CHEMICAL SPECIATION

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Characterizing the strong binding of Hg to thiol functional groups (RSH) of natural organic matter (NOM) and membranes of methylating bacteria, is essential to understand Hg speciation and availability for cellular uptake and methylation. In this study, the concentration of RSH functional groups in NOM and at the membranes of methylating bacteria (Geobacter sulfurreducens PCA and Desulfovibrio desulfuricans ND132) was determined by combined synchrotron based S XANES and Hg EXAFS. Furthermore, cysteine (Cys) was used as a competitive ligand to determine the conditional stability constant for the binding of Hg(II) to RSH groups by directly measuring the equilibrium concentration of Hg(Cys)2 using liquid chromatography inductively coupled plasma mass spectrometry. The interactions of Cys with NOM/membranes and the potential formation of hetero-ligand complexes, i.e. (RS)Hg(Cys), were examined by isotope tracing of 13C labeled Cys. The equilibrium concentrations of Cys, Hg(Cys)2 and (RS)Hg(Cys) were also determined by 1H-nuclear magnetic resonance spectroscopy (1H NMR). The results show that the conditional stability constant (log K) is similar for Hg(II) bond to RSH groups in both NOM and at membrane surfaces, with a log K in the range of 39-41 for Hg(RS)2, Hg2+ + 2RS- = Hg(RS)2. The study further provides the first evidence of potential hetero-ligand complex, with a log K of 38-40 for (RS)Hg(Cys), Hg2+ + RS- + Cys = (RS)Hg(Cys). Our results provide the fundamental thermodynamic data to model the Hg(II) speciation in complex systems with Cys, NOM-thiols and membrane-thiols of Geobacter sulfurreducens and Desulfovibrio desulfuricans. This ability is decisive to advance our fundamental understanding of how Hg(II) interactions with such different thiols control Hg(II) bioavailability and rates of methylation.

MO-019

IMPACT OF ORGANIC MATTER AND ENVIRONMENTAL VARIABLES ON THE DISTRIBUTION OF HG AND MEHG AND NET METHYLATION IN COASTAL SEDIMENTS ALONG THE US EAST COAST.

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The role of organic matter in controlling the methylation of mercury (Hg) in sediments is not fully understood. The binding of Hg to organic matter (OM) in the sediment has been suggested to limit the bioavailability of Hg to methylating bacteria, and thus its methylation. Labile organic matter, on the other hand, could stimulate the activity of Hg methylating bacteria and mercury methylation. Also, Hg complexed to dissolved organic molecules has been shown to be directly available for uptake by Hg methylating bacteria in pure culture studies but has not been shown in natural systems. We therefore studied the role of particulate and dissolved organic matter (POM and DOM, respectively) in influencing the methylation of Hg in two separate field campaigns on the east coast of the US. In 2013, bulk and porewater Hg and MeHg and ancillary parameters were determined and methylation assays were conducted using intact sediment cores sampled at 6 locations with sub-sites of high and low organic matter content. The DOM in the porewater was also characterized with fluorescence spectroscopy. In 2015, another 12 sites were sampled for similar parameters and methylation assays were conducted using sediment slurries with tracers added as different solid (micro and nanoparticulate β-HgS and POM) and dissolved inorganic Hg complexes. For the sediments, the concentration and log KD for HgT correlated positively with %LOI while %MeHg was negatively correlated. Though these results support the notion that binding of Hg to sediment with high OM inhibits methylation, the species-specific tracers used in the 2015 study demonstrate that the binding of Hg to high and low OM sediments limits HgII methylation similarly. Thus, the higher methylation typically seen in low OM sites may be related to the influence of OM quality on bacterial methylating activity. Using the species-specific tracers, we show for the first time that HgII complexed to DOM under natural conditions was directly available for uptake by methylating bacteria in the sediment. In addition to assessing the role of OM on mercury methylation, we will also discuss the impact of environmental variables on the distribution of Hg and MeHg across the estuaries. These results are critical for understanding and modelling the impact of changing anthropogenic inputs and climate change on the concentrations of Hg and MeHg in the environment.

MO-020

EFFECTS OF THIOL LIGANDS ON MERCURY CELLULAR SORPTION, BIOAVAILABILITY, AND METHYLATION BY ANAEROBIC BACTERIA

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Microbial conversion of inorganic mercury (Hg) to methylmercury (MeHg) is a significant environmental concern because of the bioaccumulation and biomagnification of toxic MeHg in the food web. Recent genetic discoveries have identified that only a small group of microorganisms is capable of producing MeHg in anaerobic environments, but factors affecting Hg bioavailability and thus MeHg production remain unresolved. In this presentation, we systematically evaluate Hg uptake and methylation by representative Hg methylators such as Desulfovibrio desulfuricans ND132 and Geobacter sulfurreducens PCA and the roles of complexing organic ligands on Hg sorption and methylation. Cell sorption or complexation, reduction, oxidation, and methylation of Hg are found to occur concurrently but vary greatly, depending on specific microbial strains and their relative binding affinities with Hg. Strong cellular sorption results in a large fraction of the Hg unavailable for methylation. The presence of thiol ligands such as cysteine competes with cells for Hg uptake but, over time, promotes Hg methylation by increasing Hg bioavailability or decreasing cellular Hg sorption. D. desulfuricans ND132 cells show a higher binding affinity with Hg than G. sulfurreducens PCA cells, and all thiols (i.e., cysteine, glutathione, and penicillamine), added either simultaneously with Hg or after cells have been incubated with Hg, substantially increase MeHg production. However, for G. sulfurreducens PCA cells, only cysteine results in increased MeHg production over time. Cells do not appear to preferentially take up Hg-thiol complexes, but Hg-ligand exchange between thiol complexes and the cell-associated proteins likely constrains Hg uptake and methylation. We suggest that, aside from aqueous chemical speciation of Hg, binding and exchange of Hg between cells and complexing ligands such as thiols and naturally dissolved organics in solution are important controlling mechanisms of Hg bioavailability, which should be considered when predicting MeHg production in the environment.

MO-021

LINKING MICROBIAL ACTIVITY AND HG BIOAVAILABILITY TO HG METHYLATION IN LAKE TITICACA HYDROSYSTEM (BOLIVIAN ALTIPLANO)

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In aquatic ecosystems, the neurotoxic Hg compound, monomethylmercury (MMHg), can be produced in many places including sediments, water columns, biofilms and periphytons but their respective production rates are barely compared within one ecosystem. In this work, we concomitantly investigated the transformations of Hg species (methylation and demethylation) in various compartments from high altitude tropical lakes located in the Titicaca hydrosystem (Bolivian Altiplano, 3600-3800 m a.s.l.). Five sites representative of the different settings of these lakes (shallow vs deep, pristine vs eutrophicated or contaminated) were selected to constrain the role of sediments, periphyton associated to aquatic plants (Totoras) or green algae (Charace) and benthic biofilms in MMHg production, degradation and accumulation. Incubation experiments with enriched isotopic tracers were carried out during two field campaigns at the end of the rainy and dry seasons in 2014. Organisms involved in Hg transformations were first constrained by using inhibitors targeting specific biological activities (sulfate-reduction, photosynthesis and methanogenesis). The bacterial diversity of present and active communities was also evaluated along time-course experiments together with extracellular sulfides and low molecular weight thiols acting as ligands regulating Hg transformations. Intense MMHg production was found in benthic biofilm and green algaes periphyton with methylation rate constants (Km) up to 0.2 and 0.1 d-1, respectively. On the contrary, Km in sediments and plant periphyton remains low (0.01 and 0.001 d-1, respectively). Demethylation rate constants (Kd) were found to vary between the compartments and according to the conditions but remained overall in the same range (0.2 - 0.6 d-1). Sulfate reducers were clearly identified as the main methylators in these lakes and the variability in Km observed between the different compartments is first explained by the presence or absence of bacterial genera for which methylating strains have been identified. Secondly, a great diversity of extracellular low molecular weight thiols was found to be produced by both benthic biofilms and green algaes periphyton, which also explain the high methylation extents observed owing to their influence on Hg bioavailability. This study provides a first assessment of the relative importance of each compartment for MMHg production and release into such freshwater ecosystems and demonstrates the combined influence of bacterial diversity and activities and extracellular ligands on the transformations of Hg species.

MO-022

DIFFUSIVE GRADIENT IN THIN-FILM PASSIVE SAMPLERS AS INDICATORS OF MERCURY BIOAVAILABILITY FOR BIOMETHYLATION IN SEDIMENTS

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Mercury (Hg)-contaminated sediments comprise a variety of chemical Hg species, yet only a small fraction of the total Hg is generally bioavailable to microorganisms that produce monomethylmercury (MeHg), a potent neurotoxin. Diffusive gradient in thin-film (DGT) passive samplers are widely used for in-situ quantification of trace metal concentrations in surface waters and metal bioavailability to benthic invertebrates, but DGTs have not been tested for their ability to predict Hg bioavailability to methylating microbial communities. The objective of this study was to test the efficacy of DGT samplers with a series of anaerobic estuarine sediment slurry microcosms. The microcosms were amended with multiple, isotopically labelled endmembers of inorganic Hg ($^{04}\text{Hg}^{+}$, ^{96}Hg-humic acid, ^{99}Hg-sorbed to FeS, ^{00}HgS nanoparticles) with a known range of bioavailability and methylation potentials. The net production of MeHg from each endmember was quantified as the slurries were incubated from 0.5 to 5 days. We also employed various measures of Hg reactivity, including cumulative uptake into the DGT sampler, the 0.2-mm filter passing fraction of Hg, and the extractable fraction of Hg (as determined by selective extraction with glutathione). The net production of MeHg (as a % of the total Hg of each endmember added) was generally greater for the dissolved endmembers than the particulate endmembers, as expected. For each time point in the incubation, the percentage of Hg uptake in the DGT from each endmember correlated with the %MeHg. In contrast, the concentrations of filter-passing Hg and the extractable fraction of Hg (as determined by a glutathione selective extraction) did not correlate with %MeHg values. These results indicate that the data provided by DGT samplers could be used to assess microbial Hg bioavailability in sediments. Furthermore, polymerase chain reactions performed with DNA extracted from slurries and with primers developed for the quantification of the gene hgcA responsible for the methylation of Hg in Deltaproteobacteria, indicated the presence of these organisms in the slurries.

MO-023

QUANTUM CHEMICAL INSIGHTS INTO DIMETHYLMERCURY FORMATION ON REDUCED SULFUR REVEAL COMMON THEMES IN MERCURY METHYLATION AND DEMETHYLATION

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Unlike monomethylmercury (MeHg+), which is produced primarily by anaerobic microorganisms, the origin of dimethylmercury (Me2Hg) in the environment remains a mystery largely because its extreme toxicity understandably deters experimental efforts. Recent, careful experiments have shown that MeHg+ adsorbed onto surfaces bearing reduced sulfur (Sred) groups, e.g., sulfide minerals and thiol-rich cell membranes, can be converted to Me2Hg (Jonsson, S. et al. Sci. Rep. 2016, 6, 27958). Here, we circumvent hazards associated with working with toxic Hg species by using density functional theory calculations to investigate the roles of sulfide and mono- and dithiols in mediating transmethylation of two MeHg+ to form Me2Hg and inorganic Hg(II). We find that the binding of two MeHgSred units at adjacent Sred sites facilitates methyl ligand exchange, which, depending on the Hg:Sred ratio, molecularity and conformational flexibility, may be either concerted or stepwise via an unusual dinuclear Hg(II) complex. We also quantify the strength of the HgC bond under different thiolate coordination environments. We compare and contrast these findings with the proposed mechanisms of MeHg+ demethylation by MerB and Hg methylation by HgcA.

MO-024

SUBMERGED VEGETATION AFFECTING BIOAVAILABILITY OF MERCURY IN SEDIMENTS

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Background/Objectives: Submerged macrophytes are suggested to create a microenvironment favorable for bacterial activity in aquatic sediments and subsequently for methylation of inorganic mercury (Hg) into the bioavailable and bioaccumulating organic species methyl Hg (met-Hg). The aim of the study was to investigate how presence of submerged macrophytes affects sediment methylation and bioavailability of met-Hg in a brackish, land-locked fjord in the temperate zone of southeast Norway. The fjord has received substantial amounts of Hg since the early 1900s due to industrial discharges. Despite heavily contaminated sediments, the fjord hosts a large submerged meadow of macrophytes.

Approach/Activities: We sampled sediment cores within and outside a submerged meadow and grab samples were collected along a 150 m transect reaching from shallow vegetated waters (approx. 2 meters) into deeper non-vegetated waters (approx. 4 meters). Total Hg (tot-Hg) and met-Hg were measured in sediment core profiles and in grab samples, as well as in pore water extracted from the sediment grab samples. In addition, profiles of supporting sediment characteristics were investigated in the cores. Flux of Hg from sediments to water were investigated in box core samples collected within and outside the meadow. Finally, macrophytes were sampled monthly from May until September 2015, and concentrations of Hg were measured in different sections of the macrophytes.

Results/Lessons Learned: Our results revealed higher methylation rates (expressed as met-Hg to Hg ratio) in sediments and higher flux of met-Hg within the meadow compared to outside. Favourable conditions for methylation and peak met-Hg concentrations coincided with the rhizosphere within the meadow. In macrophytes, higher Hg-concentrations were found in roots and leaves compared to stem, indicating uptake in roots and bioaccumulation in roots and leaves. Hence, the study is in support of the hypothesis that macrophytes influence the bioavailability of Hg in sediments, due to improved conditions for bacterial activity, whereas macrophytes may act as vectors for Hg into aquatic food webs due to uptake and accumulation of Hg from sediments.

3c-1: Risk assessment of mercury exposure to fish, birds, and wildlife

MO-025

CURRENT RESEARCH STRATEGIES WILL PRODUCE MERCURY TOXICITY REFERENCE VALUES THAT DO NOT PROTECT AVIAN POPULATIONS FROM HARM

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Assessing risk to a wildlife population from a toxicant is generally done in one of two ways. Researchers may compare the tissue concentrations, health, or reproductive success of populations at contaminated and reference sites. Alternately, dosing may be carried out on a model species in captivity to measure effects on reproductive success or physiological condition. Both methods have generated a wealth of knowledge on the mechanisms through which mercury harms wildlife, and the scale of this global problem. However, both research strategies are likely to underestimate the effects of the contaminant and to suggest toxicity reference values that are not protective of typical populations. This is because when studying natural populations exposed to environmental contaminants, researchers are studying only the surviving lineages, which likely have experienced strong natural selection for contaminant resistance. This problem can be eliminated by experimentally exposing naïve subjects in the laboratory. However, the lives of laboratory animals lack many of the stressors facing their wild counterparts, such as predation, competition, weather, and challenges that require cognition to overcome (e.g., the need to remember spatial locations). Thus, contaminant exposure in captivity may fail to cause harm at levels that would be deleterious in the wild. Using data from recent studies on mercury-exposed songbirds illustrates these points. Avian mercury toxicity reference values, recently argued by some to be too low, are likely too high if they are derived from resistant wild populations or captive animals with unchallenging lives. For more accurate results, dosing studies on captive animals should provide housing conditions with multiple challenges such as temperature fluctuations, competition for mates and hidden food. Dosing could also be attempted on free-living animals at uncontaminated sites, which circumvents the problem of studying resistant populations. At contaminated sites, new populations of non-resistant individuals can be recruited, for example by using nestboxes to attract tree swallows to habitats that did not support them beforehand. All of these techniques are more difficult and expensive than current methods, but if we are interested in identifying meaningful effects thresholds, continuing with the current strategy is imprudent.

MO-026

SONG SPARROWS AS RIPARIAN BIOSENTINELS OF MERCURY POLLUTION AND METHYLATION IN THE SAN FRANCISCO BAY AREA (USA)

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High levels of mercury in the San Francisco Bay region pose a threat to local wildlife. Recent studies have documented unexpectedly high concentrations of methylmercury in terrestrial invertivores indicating possible risk from exposure via the food web. Such discoveries prompted interest in developing a biosentinel for methylmercury in stream riparian food webs of the Bay Area. The Song Sparrow (Melospiza melodia) was determined to be the best riparian biosentinel candidate on the basis of its natural history, sampling feasibility, and sensitivity to mercury. The ability of Song Sparrows to reflect a wide range of mercury concentration in their blood, and thereby reflect differences in methylmercury risk between areas, was assessed by sampling individuals from riparian sites across the region. The sampling design was based on a conceptual model in which the key drivers of biosentinel exposure were Total Mercury Contamination of sediment (Total Mercury Contamination) and physicochemical environmental conditions associated with production of methylmercury (Net Methylation Environment). Net Methylation Environment was assumed based on landscape-level indicators. Both Total Mercury Contamination and Net Methylation Environment were found to influence biosentinel mercury concentrations. Results of this study confirmed the appropriateness of the Song Sparrow as a riparian mercury biosentinel species.

MO-027

MONITORING SPATIAL GRADIENTS AND TEMPORAL TRENDS OF MERCURY IN SONGBIRDS OF NEW YORK STATE

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Mercury (Hg) contamination in aquatic and terrestrial ecosystems is a widespread issue that poses considerable reproductive, behavioral and physiological risks to wildlife populations. Songbirds are now recognized as indicators of mercury in terrestrial ecosystems, where invertivore foodwebs biomagnify methylmercury (MeHg) to levels that can adversely affect reproductive success. With upcoming changes to Hg emissions regulations, understanding how MeHg bioavailability currently varies across the landscape is important for quantifying the effects of these changes. Building upon 13 years of mercury research in New York State, a five-year project was initiated in 2013, to identify at-risk songbird species, classify sensitive habitat types, and to assess spatial and temporal trends of mercury across a variety of ecosystems. To date, approximately 1,900 blood and feather samples have been collected and analyzed from songbirds across the state. This project focuses on: (1) annual sampling and monitoring at established study sites to evaluate temporal patterns in songbird mercury exposure; (2) sampling selected sites statewide to identify mercury hotspots for inclusion into a predictive map documenting spatial gradients of methylmercury availability; and (3) analysis of museum specimens to quantify trends in Hg exposure over the 20th Century.

MO-028

ENDURANCE FLIGHT ABILITY IN A MIGRATORY SONGBIRD IS REDUCED BY EXPOSURE TO DIETARY METHYL-MERCURY

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There is ample evidence that methylmercury (MeHg) exposure can cause reductions in avian fitness, particularly in aquatic species during breeding. However, recent work indicates that terrestrial songbirds that live in association with MeHg contaminated environments can bioaccumulate MeHg to high levels in body tissues . How elevated MeHg levels in migratory songbirds affect flight performance and migration is still unknown. We conducted a MeHg dosing experiment (target concentration: 0.5 ppm and 1 ppm (w.w.) actual concentration: 0.38 ± 0.04 ppm and 0.73 ± 0.08 ppm, w.w.)with yellow-rumped warblers (Setophaga coronata) while they were in a hyperphagic, migratory state. Warblers rapidly bioaccumulated dietary MeHg by 20-fold in blood

(w.w.), 40-fold in brain and muscle (d.w.), 60 fold in liver (d.w.), and over 100 fold in kidneys (d.w.) after 2 weeks. These increases in MeHg concentrations did not affect vertical takeoff, but in two-hour wind tunnel flights, MeHg treated warblers had a greater median of numbers of strikes (landing or losing control) in the first 30 minutes, longer strike duration, and shorter flight duration than control birds. In MeHg treated warblers, the number of strikes in first 30 minutes was related to blood Hg concentration in a sigmoid, dose-dependent fashion with threshold near 11 ppm. From our results, we conclude that hyperphagic migratory birds rapidly accumulate MeHg from the diet, which can subsequently lead to decreased flight performance and migratory endurance.

MO-029

MERCURY AS AN ALTERNATE FOR GENETIC SPECIES IDENTIFICATION OF ALBATROSS (PHOEBASTRIA SPP.) EGGS FROM MIDWAY ATOLL

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The National Institute of Standards and Technology (NIST) Seabird Tissue Archival and Monitoring Project (STAMP) expanded to the Pacific Islands Region in 2010 and began collecting Laysan albatross (*Phoebastria immutabilis*) and black-footed albatross (*Phoebastria nigripes*) eggs from the Northwestern Hawaiian Islands (NWHI) on Midway Atoll in 2011. Laysan albatross and black-footed albatross are sympatric, synchronous breeders that nest in dense colonies on Midway Atoll. Abandoned, non-viable eggs were collected by USFWS staff and volunteers. Definitive species identification of abandoned albatross eggs can be difficult on NWHI due to close nesting colonies and visually indistinguishable eggs between species resulting in some uncertainty of the egg species by field collectors. The original intent of this study was to determine mercury concentrations in eggs of albatross species for Midway Atoll. Total mercury was measured by atomic absorption spectrometry (AAS) in an aliquot of the homogenized egg content from each albatross egg collected (n = 57) from 2011 to 2013. Mercury analysis showed significantly ($p < 0.001$ ANOVA) greater concentrations in black-footed albatross eggs compared with Laysan albatross eggs, with some notable exceptions, raising questions about the accuracy of species identification in the field. Since species identification of some eggs was questionable and the species for several eggs were not identified, genetic analysis was performed on eggshell membranes where DNA was recoverable (n = 50). Genetic species identification matched suspected species based on mercury concentrations with 100 % accuracy. Trace element concentrations have been used as an alternate for genetics in other species such as fish for population structure delineation. Mercury may therefore serve as an alternate method of species identification for sympatric breeding albatross species that have significantly different concentrations due to prey and foraging grounds differences when genetic material is not available. Since mercury is routinely measured in STAMP eggs, this would be an attractive alternative to expensive genotyping. To test whether mercury can serve as an alternative to genotyping for NWHI albatross eggs, albatross eggs collected (n = 41) on Midway Atoll in 2014 and 2015 are currently being measured for mercury.

MO-030

MERCURY EXPOSURE AND IMPACTS IN BALD EAGLES IN THE PENOBSCOT RIVER WATERSHED, MAINE.

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We evaluated dietary Hg exposure in Bald Eagle (Haliaeetus leucocephalus) nestlings throughout Maine's Penobscot River watershed in 2004 – 2015, focusing particularly on exposure relative to the location of a significant Hg point source (HoltraChem) located in a brackish portion of the Penobscot River. The Penobscot River watershed encompasses more than one-quarter of the state, stretching over 150 km from northern lakes to an estuary and Penobscot Bay. Geometric mean Hg concentrations in nestling blood (range 0.06 – 1.51 µg/g) and feathers (range 2.9 – 46.8 µg/g) varied significantly across the four major habitat types in the study area ($p < 0.05$). Means generally followed the pattern: lakes > freshwater rivers > brackish rivers > marine. The overarching influence of habitat type on Hg exposure in Bald Eagle nestlings masked detection of the possible influence of Hg exposure attributable to HoltraChem. We also compared reproductive measures (productivity, young fledged / occupied nest; nest success, proportion of nests successfully fledging ≥1 young) to eagle tissue Hg concentrations and will discuss those relationships and influential factors. Bald Eagle tissue Hg concentrations found in lakes and freshwater rivers in the Penobscot River watershed are similar or higher than virtually all comparably sampled Bald Eagle populations elsewhere. Eagles at lakes in the Penobscot River Watershed were most similar to a site in BC Canada associated with a Hg mine. In contrast, eagle sampling sites below HoltraChem, one of the most substantial Hg pollution point sources in the country, exhibited relatively low concentrations of Hg due to the predominant influence of factors associated with habitat type. We attribute the notable exposure of Hg in lake- and freshwater river-dwelling Bald Eagles in the Penobscot River watershed upstream from HoltraChem to the combined influences of atmospheric deposition, other point sources, and site-specific biogeochemical factors. Bald Eagles have been repeatedly proven to be valuable contaminant bioindicators at site-specific and watershed scales in both freshwater and marine ecosystems; however, eagles' large home range and dietary plasticity limits their use in smaller scale, traditional 'upstream vs. downstream' contaminant risk evaluations, particularly those spanning multiple habitat types.

MO-031

MODELLING FUR AS A NON-INVASIVE BIOMARKER FOR ENVIRONMENTAL MERCURY EXPOSURE

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Mercury (THg) is a pollutant of global concern. Sentinel species, such as river otter and mink, are often used to monitor environmental concentrations. Tissue THg concentrations are often used as biomarkers of exposure. However, there is no comprehensive model relating mercury tissue concentrations in different tissues, making inter-study comparisons challenging. Our objective is to establish universal conversion factors relating fur, brain, liver, kidney, and muscle THg tissue concentrations using mean concentrations and standard errors reported in literature. Data from over 6000 samples, pooled across 16 studies, and 96 sampling sites in North America and Europe were used. A total of 16 regressions were derived for the river otter and mink models which were statistically significant at a 95% confidence interval and yielded high explained variance. The models were validated using an external data set of individually measured THg tissue concentrations. The validated conversions were used to evaluate the current 20 μg/g and 30 μg/g fur mercury screening guideline. At both of these fur concentrations, brain concentrations are of concern for altering brain neurochemistry. We suggest a more conservative 15 μg/g fur mercury screening guideline to protect more sensitive furbearers. The model conversion factors can be used to predict internal organs from fur, thus eliminating the need to collect invasive tissue samples (e.g. brain or liver) for future monitoring programs.

MO-032

METHYLMERCURY TOXICITY REFERENCE VALUES FOR MAMMALIAN WILDLIFE POPULATIONS: CRITICAL REVIEW AND ANALYSIS

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We reviewed effects of chronic methylmercury exposure on non-primate mammals, with the goal of identifying toxicity reference values for the ecological risk assessment of mammalian wildlife populations. The review focused on dietary exposures in which effects on reproductive success or survival were investigated. Issues related to applying toxicity study results in ecological risk assessments were also reviewed. Relevant toxicity data were available primarily for mink and rats. Dose-response relationships and effect thresholds will be summarized. In contrast to birds, mink exhibited little difference in sensitivity between survival and reproductive endpoints, suggesting that methylmercury effects on reproductive success may be secondary to more general systemic toxicity. Important considerations in applying the available mammalian toxicity data include interspecies differences in mercury tolerance adaptations, mercury-selenium interactions, methylmercury bioaccessibility, and effects of body weight differences on dose extrapolation. Marine mammals are well adapted to demethylate, sequester, and eliminate mercury; data to quantify methylmercury exposure levels that would overwhelm these tolerance mechanisms remain elusive. Susceptibility of bats to methylmercury toxicity is a matter of increasing interest, and uncertainties in dose extrapolation are particularly significant for bats due to their small body sizes and high food ingestion rates.

3e-1: Human exposure and health effects of mercury: epidemiology and population studies

MO-033

GENE-MERCURY INTERACTIONS AND METHYLMERCURY NEUROTOXICITY

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Individuals differ in susceptibility to methylmercury neurotoxicity, in part, due to underlying genetic differences. This presentation aims to evaluate the state-of-the-art evidence of the role of gene-mercury interactions for neurodevelopment and neurotoxicity. Genes frequently studied for influence on methylmercury neurotoxicity are mainly related to the metabolism of glutathione (a key factor for methylmercury transport and excretion), selenium metabolism (which binds to methylmercury), and nervous system maintenance (which can alter the response to methylmercury toxicity), but the results have been inconclusive for most of the genes. We have recently investigated the role of another group of

genes, belonging to the cytochrome P450, family 3, subfamily A (CYP3A) family, in relation to mercury neurotoxicity early in life. The CYP3A genes encode liver enzymes that perform the initial chemically-modifying steps of metabolism of a number of drugs and xenobiotic compounds. Our results, based on four different mother-child cohorts (n=2639) in Europe and Republic of Seychelles with different ethnic background and varying exposure to methylmercury, suggest that functional polymorphisms in CYP3A genes may in some of the populations modify the response to MeHg exposure during early life development. So far, candidate gene approaches have not identified a major gene modifying the toxicity of mercury, suggesting that genetic susceptibility to methylmercury might be a polygenic trait and the genes involved may differ depending on population. Further research should also consider interactions between genes and interactions with nutrients to help identify subgroups that are vulnerable to mercury neurotoxicity.

MO-034

ASSOCIATIONS BETWEEN METHYLMERCURY EXPOSURE, POLYUNSATURATED FATTY ACID STATUS AND INFLAMMATION IN PREGNANCY

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Pro and anti-inflammatory cytokines have been studied in several human conditions. The differentiation of T cells into either T-helper type 1 (Th1; pro-inflammatory) or T-helper type 2 (Th2; anti-inflammatory) cells determines the type of immune response that is required. The Th1/Th2 balance has been used to characterize dominating cytokine patterns and in normal pregnancy this is thought to favor a more anti-inflammatory Th2 response to allow tolerance of the fetus. Disruption to the Th1/Th2 balance and resulting immune response may result in an increased susceptibility to inflammatory disease and adverse pregnancy outcome. However, there is a paucity of observational human data on the immunotoxic effects of methylmercury (MeHg) exposure during pregnancy. Fish consumption is the primary source of human exposure to MeHg and also the richest dietary source of n-3 polyunsaturated fatty acids (PUFA). Previous findings from the Seychelles Child Development Study suggest that the maternal biological ratio of n-6/n-3 PUFA, another indicator of the inflammatory milieu, may modify the effects of MeHg on child development. This suggests that the immune system plays an important role in mediating potential MeHg toxicity. In order to better understand the immunomodulatory mechanisms of MeHg and their potential regulation by PUFA, we characterized an extensive panel of inflammatory markers, including cytokines from the Th1 and Th2 subsets, in maternal blood samples collected at 28 weeks gestation (n=1474) in the Seychelles Nutrition Cohort 2. The current study undertakes a novel analysis using this rich dataset to investigate associations between blood MeHg concentrations and serum PUFA status (both measured at 28 weeks of gestation) and inflammatory markers. We used linear regression analysis with both main and interactive effect models that included MeHg, PUFA and relevant covariates. Preliminary analyses indicated that the maternal n-6/n-3 ratio is positively associated, and n-3 PUFA status negatively associated, with concentrations of the pro-inflammatory marker C-reactive protein (CRP). One explanation would be the anti-inflammatory effects of n-3 PUFA in our high fish-eating cohort. We hypothesized that maternal MeHg exposure would be associated with increased pro-inflammatory markers (Th2 dominance and lower Th1/Th2 ratios) and that PUFA status would modify these associations. These results will be important to future research on how the maternal immune response might be influenced by both MeHg and PUFA and how this impacts on child development.

MO-035

THE INVERSE ASSOCIATION BETWEEN METHYLMERCURY AND DISEASE ACTIVITY IN SYSTEMIC LUPUS ERYTHEMATOSUS IS EXPLAINED BY N-3 POLYUNSATURATED FATTY ACIDS FROM FISH CONSUMPTION: AN OBSERVATIONAL STUDY

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Systemic lupus erythematosus (SLE) is a prototypic autoimmune disease with an unknown pathogenesis and a variable presentation. It is proposed that genetic predisposition and exposure to environmental factors are responsible for both the initiation of disease and the exacerbation of existing disease. One environmental factor that has been implicated in the pathogenesis of SLE is mercury (Hg) exposure. Humans are exposed to MeHg through fish consumption, and Hg0 through dental amalgams. Fish also contain n-3 long chain polyunsaturated fatty acids (LCPUFA), which have been shown to be beneficial in the management of SLE. Hair and urine samples were collected from 99 SLE patients to assess exposure to MeHg and Hg0, respectively. Patients were assessed for disease activity and disease associated damage using 4 indices; the British Isles Lupus Assessment Group (BILAG) index, the Systemic Lupus Activity Measure (SLAM), the Safety of Estrogens in Lupus Erythematosus National Assessment Systemic Lupus Erythematosus Disease Activity Index (SELENA SLEDAI), and the Systemic Lupus International Collaborating Clinics/American

College of Rheumatology (SLICC/ACR) damage index. Standard multiple regression identified a significant inverse relationship between hair Hg and BILAG (β= -0.231, p= 0.046, 95% confidence interval (CI): -0.422, -0.004) albeit, controlling for total serum n-3 LCPUFA negated this finding (β= -0.222, p= 0.059, 95% CI: -0.416, 0.008). Furthermore, SLAM was inversely correlated with serum EPA status (r= -0.247, p= 0.016), DHA status (r= -0.262, p= 0.011), total n3 (r=-0.302, p=0.003) and fish intake (r= -0.335, p= 0.032). There was no association between urinary Hg and any measure of disease activity or disease associated damage. The findings from this study suggest that low level MeHg and Hg0 exposure is not adversely associated with disease activity or damage in SLE. The inverse association of hair Hg with BILAG in SLE patients appears to be explained by the co-exposure to n-3 LCPUFA present in fish.

MO-036

FISH CONSUMPTION, MERCURY LEVELS, AND AMYOTROPHIC LATERAL SCLEROSIS (ALS).

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Background: Mercury is a neurotoxic metal that has been found in some studies to be a risk factor for amyotrophic lateral sclerosis (ALS). The primary source of U.S. population exposure to mercury is via consumption of methylmercury-contaminated fish.

Objective: To assess in a case-control study the risk of ALS associated with mercury intake via fish / seafood consumption, and with mercury intake measured as concentration in nails.

Methods: We used questionnaires to assess fish and seafood consumption in a case-control study of ALS (N=294 cases, 224 controls). We estimated annual methylmercury exposure among fish / seafood consumers by cross-referencing self-reported consumption with the corresponding fish fillet mean methylmercury concentrations. We used inductively coupled plasma mass spectrometry to measure levels of mercury in toenail samples obtained from ALS patients, compared to those of controls without neurodegenerative illness. Odds ratios (OR) were adjusted for age and gender.

Results: Consumption of the fish caught was associated with increased risk of ALS (OR 2.2 95%CI 1.1-5.0), though angling per se was not (OR 1.1 95%CI 0.7-1.7). Among patients regularly consuming fish, those in the top quartile for estimated annual methylmercury intake were at a 2-fold increased risk of ALS, compared to those with lower levels. Using toenail mercury concentrations as a biomarker of exposure, there was a statistically significant increased ALS risk associated with toenail mercury level (P=0.036).

Conclusions: These data demonstrate that the risk of ALS is associated with fish and seafood consumption. Both estimated fish-related mercury intake and biomarker data suggest mercury exposure is a risk factor for ALS.

MO-038

PRENATAL EXPOSURE TO MERCURY AND EPIGENOMIC MODIFICATIONS ASSOCIATED WITH NEURODEVELOPMENT

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Background: Mercury is a worldwide environmental contaminant that persists and bioaccumulates as methylmercury in the food chain. Prenatal exposure to mercury, typical of regular fish consumption, is associated with lower cognitive performance in childhood. Disruption of fetal epigenetic programming could explain mercurys neurotoxicity.

Methods: Within Project Viva, a US pre-birth cohort, we examined associations of maternal 2nd trimester red blood cell mercury concentrations and epigenome-wide DNA methylation differences in 321 cord blood samples at a single nucleotide resolution using the Infinium HumanMethylation450 BeadChip, and evaluated the persistence of the associations during early (2.9 to 4.9 years) and mid-childhood (6.7 to 10.5 years). Additionally, we examined the association of prenatal mercury with blood global 5-hydroxymethylcytosine (%-5hmC) and global 5-methylcytosine (%-5mC) DNA content at birth, early childhood and mid-childhood.

Results: Among males, a doubling in prenatal mercury concentration was associated with 2.4% lower regional cord blood DNA methylation (95% CI: -3.8, -1.0) at nine CpG loci within the Paraoxonase 1 gene (PON1). Cord blood methylation at the PON1 locus predicted lower cognitive test scores measured during early childhood. The association between prenatal mercury exposure and DNA methylation at the PON1 region was persistent in early but not mid-childhood blood. Similarly, a doubling in prenatal mercury exposure was associated with 0.015% lower 5hmC global genomic content of cord blood for all infants (95% CI: -0.03, -0.0002) and this association persisted in early but not mid-childhood blood.

Conclusions: Prenatal mercury exposure was associated with lower regional PON1 DNA methylation as well as lower global 5hmC DNA content at birth. These associations were persistent in early but not mid childhood blood. Our results highlight the potential role of epigenetic programming as a target of prenatal mercury exposure and suggests that effects of prenatal exposure might be malleable during childhood.

MO-039

POSTNATAL METHYLMERCURY EXPOSURE AND NEURODEVELOPMENT IN THE SEYCHELLES CHILD DEVELOPMENT STUDY MAIN COHORT

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Fish consumption guidelines have relied on studies of prenatal methylmercury (MeHg) exposure from a high seafood diet during pregnancy and childrens outcomes but they do not adequately consider evidence specific to fish intake in children and adolescents. The brain is not fully developed until halfway through the third decade of life and is therefore potentially susceptible to MeHg exposure well beyond the fetal period. It is therefore critical to determine whether childrens exposure to MeHg from eating fish is associated with adverse developmental consequences. MeHg exposure from fish consumption during childhood has not been well studied to date; studies have not been specifically designed to study postnatal MeHg exposure. Thus, it is currently not known if there are adverse neurodevelopmental consequences associated with MeHg exposure when children consume fish. For nearly three decades the Seychelles Child Development Study (SCDS) has investigated the impact of prenatal MeHg exposure from fish consumption during pregnancy on child development. In 1989-1990, we recruited a cohort of 779 mother-child pairs (Main cohort). Cohort children were examined ten times for developmental outcomes from 6 months to 24 years of age and no consistent adverse associations were found with prenatal MeHg exposure. In contrast, recent postnatal MeHg exposure measured in concurrent hair samples at eight of the ten examinations was adversely associated with some developmental outcomes. Concurrent postnatal exposure was specifically associated with measures of psychomotor and executive function, attention, and general intelligence at 9 years of age and older. These cognitive domains have their greatest development postnatally and therefore may be the most susceptible to effects of postnatal MeHg exposure. We hypothesize that greater accumulated postnatal exposure is adversely associated with neurodevelopmental outcomes in later childhood, adolescence and young adulthood. We leverage the archived data to examine three cumulative postnatal MeHg exposure metrics (early life, late adolescent, and lifetime) in relation to cognitive domains that have shown adverse associations in cross-sectional analyses. Longitudinal models evaluate the consistency of associations with neurodevelopmental outcomes over time. Studying the association between postnatal MeHg exposure and neurodevelopmental outcomes is of substantial public health significance because billions of people, including children, depend daily on the nutritional properties of fish. This study provides the most comprehensive scientific assessment to date of the risks or safety of fish consumption in childhood.

MO-040

STRUCTURAL EQUATION MODEL APPLIED TO COGNITIVE ASSESSMENT OF RIPARIAN SCHOOLCHILDREN FROM THE WESTERN BRAZILIAN AMAZON.

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Several studies suggest that exposure to Methilmercury may affect children's cognitive development. Brazilian Amazon riparian population are exposed to MeHg through fish consumption. The main aim of this study is to evaluate the relationship of exposure to MeHg and children cognitive status. This study is part of the Mercury Health Impact Project, in an region where two Hydroelectric Power Plant were built in Amazon. This is a cross-sectional study with a sample of 165 riparian schoolchildren, living along the Madeira River, in the Amazon Basin. Several cognitive tests were performed by psychologists to measure children's abilities on the following cognitive domain: intelligence, memory, motor function, attention and executive function. An interview questionnaire was used to collect information on socio demographic characteristics, fish-eating habits, neurological symptoms and other relevant information. The multivariate technique structural equation modeling was used to construct a cognition's latent variable as well as to estimate its relationship with hair mercury (Hg) levels, health indicators, nutritional habits and socioeconomic characteristics. The majority of children presented Hg concentration in hair higher than 2µg/g. The average concentration was 3.3µg/g and the maximum value was 21.8µg/g. The domains that most contributed to the cognition response were memory, motor function, attention and executive function. The results showed negative effect between Hg concentration in hair and children cognition. Variables associated ($p\text{-value}<0.10$) with cognition status were hair Hg levels, family income, fish and Brazil nuts intake, parents degree of relatedness, and neurological symptoms. In conclusion, these results suggest that the higher children Hg levels, the worse is its cognitive performance, taking into account nutritional habits and individual characteristics.

4e: Understanding implications of the Minamata Convention: Now and in the future

MO-041

THE MINAMATA CONVENTION ON MERCURY – WORKING FOR A SAFER WORLD

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The Minamata Convention on Mercury was adopted in October 2013 and has been signed by 128 countries. The Convention is expected to enter into force early in 2017 after 50 countries commit to follow the obligations of the Convention. Obligations under the Convention include restrictions on the export of mercury by Parties, phasing out certain mercury-added products and stopping the use of certain processes that use mercury. Emissions of mercury to air from specified sources, and releases of mercury to land and soil are controlled under the Convention. There are obligations in relation to storing mercury prior to its use, on how mercury waste is managed and also on the management of contaminated sites. The Convention includes provisions for financial resources, capacity building, technical assistance and technology transfer, as well as the establishment of a compliance and implementation committee which will consider cases where countries may not be following the Convention requirements.

As Governments implement the Convention, their actions will decrease the anthropogenic emissions and releases of mercury. Supporting Governments in these actions require not only financial support but also expert guidance. This is being provided through the development and agreement of guidance documents, which can assist countries in taking decisions on the best actions at the national level. Experts have worked on these guidance documents, which will be formally adopted by the Conference of the Parties. The contributions of the scientific community to such documents, as well as to other implementation support activities, ensures that recommendations have scientific validity, while the involvement of the relevant industry assists with ensuring practicality and a rapid take-up of measures.

Over time, the actions will reduce the environmental burden of mercury; however the timeframes involved may be very long. Direct effects on human health may be seen more rapidly in communities such as those involved in mining activities, or those affected by point sources of pollution, where local pollution levels may be high and effects may be seen more immediately. Tracking the levels of mercury in the environment and in populations will contribute to an assessment of the effectiveness of the Convention in addressing the mercury challenge, as well as assisting to have a safer world. The scientific community will have a role to play in these activities, and, working with government, industry and the environmental community will have the best opportunity to save the world from mercury.

MO-042

THE GLOBAL MERCURY PARTNERSHIP AS A TOOL FOR SUPPORTING IMPLEMENTATION OF THE MINAMATA CONVENTION THROUGH ARTISANAL AND SMALL-SCALE GOLD MINING NATIONAL ACTION PLANS

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The Global Mercury Partnership is a voluntary, multi-stakeholder organization dedicated to the protection of human health and the environment by reducing mercury pollution. Established by the United Nations Environment Programme Governing Council, the Partnership consists of seven areas which correspond to the major industrial sectors where mercury is used or released into the environment. An eighth partnership area focuses on the environmental fate and transport of mercury. By bringing together scientists and policymakers, and by generating objective science-based assessments, the Partnership played a critical role in the negotiations of the Minamata Convention on Mercury. The activities of the Partnership are now focused on assisting countries ratify and implement the Minamata Convention through data sharing, awareness-raising, information exchange, and capacity building. In response to calls from governments and other stakeholders, the Partnership will continue its focus on bringing together scientists, experts, and policymakers, and is seeking additional ways to keep the policy community abreast of the latest scientific research and its implications for the Minamata Convention. The Partnership also seeks to forge closer ties with the scientific community to help direct researchers to policy-relevant questions and methods of effectively communicating results to policymakers.The Global Mercury Partnership is a voluntary, multi-stakeholder organization dedicated to the protection of human health and the environment by reducing mercury pollution. Established by the United Nations Environment Programme Governing Council, the Partnership consists of seven areas which correspond to the major industrial sectors where mercury is used or released into the environment. An eighth partnership area focuses on the environmental fate and transport of mercury. By bringing together scientists and policymakers, and by generating objective science-based assessments, the Partnership played a critical role in the negotiations of the Minamata Convention on Mercury. The activities of the Partnership are now focused on assisting countries ratify and implement the Minamata Convention through data sharing, awareness-raising, information exchange, and capacity building. In response to calls from governments and other stakeholders, the Partnership will continue its focus on bringing together scientists, experts, and policymakers, and is seeking additional ways to keep the policy community abreast of the latest scientific research and its implications for the Minamata Convention. The Partnership also seeks to forge closer ties with the scientific community to help direct researchers to policy-relevant questions and methods of effectively communicating results to policymakers.

MO-043

PRELIMINARY RESULTS AND LESSONS LEARNT OF THE IMPLEMENTATION OF MINAMATA INITIAL ASSESSMENT PROJECTS

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The Minamata Convention on Mercury is expected to enter into force in 2017. In order to facilitate the ratification of developing countries and countries with economies in transition, the Global Environment Facility, the main financial mechanism for the Convention, provided financial support through Minamata Initial Assessment projects. So far, over 90 countries have benefitted from this assistance with the earlier projects now in their finalisation stages. The UN Development Programme, the UN Environment Programme and the UN Industrial Development Organization are the agencies through which countries have accessed these funds. Out of the current 35 parties to the Convention (January 3 2016), 19 are implementing MIAs.

With the ultimate objective to ensure countries early ratification, these projects usually have four main components, 1) establishing a multi-stakeholder national mercury team, 2) undertaking a legal review to assess the implications and changes to be considered from the Conventions obligations, 3) establishing a national mercury inventory, and 4) raising awareness of the public on the dangers of mercury exposure.

For the legal assessment, a checklist was developed by the National Resources Defence Council to ensure that issues would not be overlooked. For the inventories, the UN Environment Mercury Toolkit for Identification and Quantification of Mercury Releases is being used. Furthermore, a common template was developed by UNDP to ensure consistent reporting of MIAs results across countries.

A survey on the implementation of MIAs was designed by the concerned agencies and distributed to all the executing partners. The results show interesting trends, which include: - The establishment of a multi-stakeholder mercury task force in the countries has been generally facilitated by the transformation or revival of existing chemicals management teams. - In countries with unintentional emission sources (coal-fired power plants, smelters, cement kilns, etc), specific emission factors have to be developed instead of using the default ones in the toolkit in order to better reflect local conditions. - The difficulty to control and monitor mercury and mercury-containing products import and exports increases the uncertainty of the scale of the issue nationally, especially for countries where mercury is used in artisanal and small-scale gold mining. - Mercury-containing waste has emerged as a key issue and will require clear technical guidance for its management.

In conclusion, the survey provided information on the common issues faced by the countries when preparing for ratification of the Convention but also highlighted emerging trends, which will be useful for the development of future initiatives.

MO-044

GLOBAL MERCURY SUPPLY, TRADE AND DEMAND - 2015

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In response to UNEP Governing Council decision 23/9 IV, this author prepared a report with the uninspiring title, Summary of supply, trade and demand information on mercury, which was published in November 2006. That report was a valuable resource in support of the negotiations leading up to the Minamata Convention in 2013.

Since 2006 there is enhanced awareness of mercury supply, demand and trade, there are increased resources available to support the Convention and related actions, mercury export bans have been imposed by the EU and the US, there are more and stricter regulations regarding mercury-added products, etc. However, because of all of these developments, as well as to help establish a baseline as the Minamata Convention takes effect in 2017, we need an update of the global situation. UNEP has therefore contracted this author to research and publish (for the base-year 2015) an update of global supply, trade and demand information on mercury. The research will be summarized in the proposed paper, which will include the following main elements, among others.

Sources and supply: main sources come from recovery, recycling, by-product, primary mining; in addition, major stocks of mercury (e.g., from Russia) are still available periodically; export bans shut off key mercury supply sources and caused an increase in the free market price of mercury; however, continued demand (esp. ASGM) has stimulated new mining; etc.

Global and regional trade: since the export bans were implemented, mercury trading hubs have shifted from the U.S., Rotterdam and Almadn to Singapore, Turkey and Hong Kong; there is now a free market price of mercury and a closed market price in regions with export bans, which has provided an incentive for illegal exports; measures are needed to improve the available data; etc.

Global and regional demand: other than ASGM, which is relatively insensitive to the mercury price, mercury demand for most applications is declining; however, VCM and chlor-alkali have been slow in converting to mercury-free processes; the transition away from dental amalgam has met some roadblocks; former mercury recyclers are developing mercury disposal businesses; measures are needed to improve the available data; etc.

Observations and recommendations: through MIAs and NAPs, countries are improving their understanding of their mercury challenges and how to deal with them; meanwhile they need also a better understanding of Minamata restrictions, e.g., restrictions on mercury mining, not permitting mined and chlor-alkali mercury to go to ASGM; etc.

MO-045

DEVELOPING MERCURY USE BASELINES AND MERCURY REDUCTION TARGETS IN NATIONAL ACTION PLANS FOR ARTISANAL AND SMALL SCALE GOLD MINING

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Artisanal and small scale gold mining (ASGM) is the largest source of mercury pollution in the world. Under the Minamata Convention, countries with ASGM are obligated to create a National Action Plan (NAP) to reduce, and where feasible, eliminate the use of mercury in the sector. Over 25 countries have already begun to create their NAPs and are now grappling with the practical challenges of the development of these plans for the complex ASGM sector. Despite these challenges, countries must robustly develop two elements that are critical to creating effective NAPs: (i) a mercury use baseline for the sector, and (ii) mercury use reduction targets.

The development of a mercury use baseline requires both quantitative and qualitative approaches to field data collection, coupled with extrapolation methods, to create a national-level estimate of a mercury use in ASGM. Because some production practices can be mercury intensive and others not, the baseline needs a description of the type, prevalence and geographic distribution of various ASGM production practices. These, combined with gold production estimates, are a principle element in creating a national mercury use estimate.

Mercury use baselines are fundamental for many of the other elements required in the NAPs, and in particular can be used as the basis for establishing mercury use reduction targets. With a good mercury use and practices baseline, countries can create realistic, quantitative, time-bound reduction targets that are built upon planned interventions to transition miners away from mercury-based practices. A practical challenge is that these reduction targets must also incorporate the political dimensions of government policy toward the ASGM sector.

MO-046

PUBLIC HEALTH IN ARTISANAL AND SMALL SCALE GOLD MINING COMMUNITIES: WHO GUIDANCE DOCUMENTS

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Public health strategies are required to be included in national action plans, aiming to eliminate or reduce the use of mercury in artisanal and small scale gold mining, when member states declare ASGM to be significant.

WHO with PAHO, regional offices, and collaborating centers experts have been developing a set of guidance documents to address public health in ASGM communities and to promote good practice with respect to research conducted on health impacts of ASGM. The proposed model for public health strategies includes assessment of institutional capacity and health conditions among ASGM communities; and institutional capacity to plan and implement health programs for ASGM communities exposed to a large number of different hazards, including different forms of mercury and its compounds. An overview of health hazards associated with ASGM has been developed by WHO to inform on the identification of health priorities in ASGM communities, which is recommended to be conducted as a health situation assessment. Developing public health strategies on ASGM (forthcoming 2017) provides a model process and suggested areas for intervention, as a reference to support development of public health strategies, to complement guidance for the National Action Plans being developed through the United Nation Environment Program Global Mercury Partnership area on ASGM.

Recommended interventions to strengthen health systems in ASGM communities include facilitating access to public health services units as well as strengthening of core public health capacities to detect and respond to ASGM related health issues, including mercury exposures and health effects. In addition, training material for health care providers under development by WHO will include occupational and environmental health risks, targeting mercury exposures and health effects, with attention to special groups such as children, elderly and women of reproductive age - health promotion activities for exposure prevention are a key element for capacity building.

The health sector will be involved on awareness raising and information exchange among different audiences, such as the general public, local authorities and national agencies. Information systems to support the integration of clinical and laboratory data are recommended to be implemented, targeting mercury exposure reduction in the environment and humans, and including human biomonitoring activities.

MO-047

HEALTH SECTOR PROGRESS TOWARDS IMPLEMENTATION OF THE MINAMATA CONVENTION

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In May 2014, the World Health Assembly adopted resolution WHA67.11on the role of WHO and ministries of health in the implementation of the Minamata Convention. WHO has already developed extensive resources to assist countries in the implementation of the health-related activities in the Minamata Convention, such as the preparation of short information documents, tools for action, norms and guidance, as well as documents for education and training, burden of disease estimates, fact sheets and question and answer sheets. Two in particular are guidance and technical materials to facilitate the phasing-out of materials containing mercury in the health sector, and support for the phasing-down of mercury use in dentistry. In cooperation with other international agencies, WHO supports implementation of mercury-related projects in 24 countries globally including 15 countries in African Region. Health is also an important component of Minamata Initial Assessment project in Central America. In addition, development of new sub-regional project involving six countries in WHO Europe is in process. Projects are aimed at protection of human health and the environment on Artisanal and Small Scale Gold Mining , health care waste and mercury containing wastes management; Some of the projects, such as the Minamata Initial Assessment, provide development of global mercury human biomonitoring scheme, and development of implementation framework for phasing down dental amalgam use, and phasing-out of mercury-containing devices from the health sector. To identify countries needs and priorities and organize trainings, a number of meetings were implemented at regional and country level: WHO Europe (2015), WHO PAHO (2015, 2016), WHO EMRO (2016), WHO AFRO for six countries (2016), and Armenia (2016).

To ensure further progress scientific support is necessary for developing guidance on article 16; for national laboratories capacity building for mercury human biomonitoring; and for preparing and updating training materials, including protocols for diagnosis and clinical support for ill-health associated with exposure to mercury and other hazards. Other perceived needs for technical support from national scientific communities include exchange of epidemiological information, awareness-raising, capacity-building and the development of guidance documents, especially as regards exposure assessment, HBM and the development of strategy and policy, scientific research on low-level exposure and indicators of occupational exposure effects, e.g. kidney functions impairments.

MO-048

ENVIRONMENTAL BENEFITS FROM IMPLEMENTATION OF THE MINAMATA CONVENTION IN CHINA

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Articles in the Minamata Convention have restricted almost all aspects of anthropogenic activities involving mercury pollution. Considering the links between different activities, comprehensive assessment of environmental benefits towards the implementation of convention will be based on mercury flow studies. We have found that embedded Hg transfers across production sectors via waste/byproduct flows reduce Hg releases to land, but lead tosecondary Hg emissions to air. In 2010, China's Hginput reached 2643 t and approximately 1368 t of Hg was emitted/released tothe environment (to air, 633 t; water, 84 t; and land, 651 t). By using the scenarios analysis method, we forecasted that Hg input in 2030 will be reduced to 1570 t under the accelerated control technology scenario. The forbidden of primary mercury mining, submission of mercury containing products, and improvement of mercury recycle will be the main drivers to reduce mercury input, which also contribute to the decrease of mercury emissions and releases. Mercury emissions/releases to air, water, and land will reach 282 t, 40 t, and 254 t in 2030. The application of best available technologies in convention-related sources will contribute to the largest proportion of mercury reduction of atmospheric mercury emissions. Although these technologies will increase mercury input to water and land, mercury releases to water and land will still be less than that in 2010 mainly due to stricter water pollution control and wastes disposal measures. The results and conclusions will provide valuable insights and perspectives for Parties to make national action plan and implement the convention.

2c-2: Sources and cycling of mercury in terrestrial ecosystems

MO-049

MERCURY EMISSION IN TIBETAN PLATEAU FROM YAK DUNG COMBUSTION

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Tibetan Plateau (TP) is generally known as the third pole of the world. Due to the sparse population and minimal industries, TP is considered as one of the cleanest regions of the world. Since the atmospheric environment monitoring in TP has been used for long-range transported pollutants assessment widely, the study of local atmospheric pollution sources in TP has raised a great deal of concern. Yak Dung is an important residential energy wildly used as the biomass fuel in TP for cooking and heating, which might contribute to the accumulation of pollutants in the air of the region. In order to evaluate Yak Dungs influences on mercury emission and air concentration, in this study, burning experiments were designed under local conditions. Yak dung samples were collected in a large area, ranging from southwest (Tingri) to northeast (Nagqu) TP and were analyzed under the local utilization condition. The vegetation atlas and population density are used to estimate the amount and distribution of Yak, which in turn can be used to estimate the quantity of local yak dung. The result shows that the concentration of total mercury in yak dung and total gaseous mercury in flue gas varies from place to place. Different pre-treatment technologies and dung source influence the water content, furnace temperature and the combustion process, and resulted in the differences in final mercury speciation and emission. The total amount and distribution of mercury emitted from yak dung to atmosphere in TP were estimated. More mercury is emitted from south central and east regions than other regions. Although TP is considered as ideal region representing atmospheric background, the influence of local emission from the burning of yak dung on atmospheric environment cannot be ignored.

MO-050

MECHANISM OF TRITICALE ROOT (TRITICOSECALE) UPTAKE OF HG2+: RESULT FROM A HYDROPONIC EXPERIMENT

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Accumulation of mercury in crops threats the safety of terrestrial food chain. Understanding the mechanism of plant uptake of Hg is a crucial step for managing mercury accumulation in crop. In this study, a series of hydroponic experiment was conducted in a plant growth cabinet to investigate the Hg uptake kinetic, as well as endogenous Zn2+ supply on Hg uptake by Triticale which is a major staple food crop in Asian. Results showed that the environmental temperature greatly affects the kinetic of Hg uptake into the root in a short term (20 min) Hg2+ exposure experiment. At ice-cold (<2°C) condition, a linear relationship between hydroponic Hg (Maximum Hg:) and root Hg was observed, showing a nonsaturable type of root uptake of Hg, probably corresponding to the bind of Hg2+ to cell wall. At 25°C, both linear and hyperbolic relationships were obtained where the form was shown at low endogenous Hg concentration (<5 M), the latter was shown at high Hg concentration, indicating both a nonsaturable (linear) and saturable (hyperbolic) type of root uptake of Hg, corresponding to both the bind of Hg2+ to cell wall and carrier-mediated Hg2+ across root-cell plasma membranes. The Michaelis-Menten equation was fit for the saturable data (r2=0.95), calculating the Michaelis constant (Km) of 7.7M and Maximum initial velocity (Vm) of 406 mgkg-1 DW. The effect of Zn2+ on root uptake of Hg2+ was variable. With increasing endogenous Zn2+ concentration, Hg concentration in roots decreased at low Hg level (<10 M) but increased at high Hg level (>20 M), suggesting that the increase of Zn2+ might competitively bind to cell wall against Hg2+ at low Hg level and might enhance the enzyme activities at plasma membranes by which increasing carrier-mediated Hg2+ uptake.

MO-051

MECHANISM OF THE ABIOTIC REDUCTION OF MERCURY (II) CHLORIDE ON SURFACES

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Mercury (Hg) is a ubiquitous, toxic and bioaccumulative environmental contaminant that undergoes reaction to change speciation and environmental fate. Some areas, like the Oakridge National Laboratory Y-12 National Security Complex (TN, USA), have experienced historical contamination of surrounding soils with Hg, and remediation of such sites has been complicated by poor mechanistic understanding of Hg reactions. Specifically, non-volatile Hg species in soil can undergo reduction to volatile Hg(0), which can then be lost to the atmosphere; however, the mechanism of this reaction is not known. This work used a computational study, coupled with laboratory experiments to identify a mechanism for the reduction of one environmentally relevant Hg species, mercury (II) chloride (HgCl2), in soil-like environments. Computational modelling using Gaussian software suggests that HgCl2 reduction might include a unimolecular dissociation driven by scissoring of the chlorine bonds to form Hg(0). Based on the energy of excitation suggested in these computational results, we hypothesized that ultraviolet-B (UVB; 280 320 nm) radiation would provide the energy necessary to cause the dissociation of HgCl2 to Hg(0), in the absence of a secondary electron donor. To test this, clean silica sand was spiked with an aqueous solution of HgCl2, and exposed to full spectrum radiation, while the flux of Hg(0) from this sand was quantified over time. Filters were applied to remove ultraviolet radiation, and preliminary results align with the molecular modeling data, suggesting that UVB radiation is particularly important in the reduction of HgCl2 in sand, and that this reduction will proceed with no secondary electron donor. Mechanistic understanding of these complex processes will assist in global mercury transport modelling, and may also contribute to the creation of effective remediation strategies for mercury contaminated soils.

MO-052

DIRECT MEASUREMENTS OF REACTIVE MERCURY AND GASEOUS ELEMENTAL MERCURY FLUXES FROM BACKGROUND AND CONTAMINATED SOILS

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A filter-based dynamic flux chamber method was used to measure gaseous reactive mercury (RM) and elemental (GEM) air-soil exchange. The soil materials used in this study include waste rock, heap leach ore, and tailings waste collected from industrial scale open pit gold mines in central Nevada, USA. Substrate concentrations ranged between 0.1 to 40 μg g-1 THg. Gaseous elemental mercury flux was quantified with a Tekran 2537 mercury analyzer, while cation exchange membrane (CEM) and Nylon filters were used to capture RM from the flux chamber sample lines. The CEM filters were used to quantify absolute RM concentrations, while Nylon filters were used to determine RM speciation by thermal desorption. Flux measurements were conducted for each material under wet and dry substrate conditions. The magnitude of RM flux was correlated with substrate Hg concentration, with lower Hg substrates showing negative or very small RM fluxes. Wet materials consistently showed higher positive RM fluxes compared to their dry counterparts. High substrate Hg tailings material showed RM fluxes up to 48 ng m-2 hr-1 under when wet. Initial thermal desorption analysis indicates a distinct difference in RM species deposited to lower Hg substrates and that emitted from tailings material.

MO-053

MERCURY MIGRATION AND OUTPUT FLUXES IN TYPICAL AGRICULTURAL CATCHMENT IN THREE GORGES RESERVOIR

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Agricultural catchment is an important component around Three Gorges Reservoir. Frequent human activities in this area make soil subject to erosion, and produced surface runoff can carry large amounts of soil with mercury (Hg) into reservoir, resulting in increase of Hg output from agricultural catchment and Hg load in reservoir. However, limited data were published about the Hg transportation in this area, and the runoff output fluxes from such watershed and caused contribution to Hg load in aquatic system were still unclear. Therefore, a typical small agricultural catchment in Wangjiagou, Chongqing was chosen to be the study area, aiming to: 1) study the Hg distribution in soil and analyze the effect of human activities on Hg distribution; 2) understand the characteristics of Hg migration; 3) calculate the Hg outputs from this agricultural catchment. The results showed that the Hg concentrations in soil ranged 9.47-94.57 μg kg-1 with an average of 34.23 ± 16.23 μg kg-1. Significant spatial and vertical distributions of Hg were detected with higher THg level in forest land and in surface soil (0-5 cm). Soil erosion rate was in the range of 0-904.16 t hm-2 yr-1, and the annual soil erosion amount was 5632.68 t. Surface related with very slight and extremely severe erosion occupied about 50% and 23% of entire land, respectively. Hg migration fluxes in different landscape types were estimated to be 1.5952 (garden plot), 0.9040 (forest land), 0.1648 (dry land) and 0.0032 (paddy land) kg km-2 yr-1, and the total Hg surface erosion load was predicted to be 276 g yr-1. The erosion load of Hg from forest land located in steep zones was 238 g yr-1 accounting for 86% of total Hg load. While Hg migrated from upland (garden plot, forest land and dry land) could be intercepted by wetland (paddy soil) in flat bottom of this catchment, and the erosion load was just 0.7 g yr-1 which was comparable with the measured migration fluxes (0.8 g yr-1) from the only exit situated in paddy land, suggesting that the project of terracing of sloping land around the Three Gorges Reservoir could decrease the Hg output from agricultural catchment to water of reservoir.

MO-054

MERCURY ACCUMULATION IN TOPSOIL RELATING TO ATMOSPHERIC DEPOSITION IN SEMI-ARID TEMPERATE GRASSLAND IN INNER MONGOLIA, CHINA

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Mercury (Hg), as a toxic and persistent pollutant, has a long-term impact on ecological system and human health. To briefly assess the effect of atmospheric deposition on semi-arid temperate grassland, contents of Hg and organic matter (TOC) in the topsoil and subsoil was analyzed for samples collected from 80 sites in central Inner Mongolia, China during 2012-2015. Results indicated that the Hg contents of topsoil varied from 1.08 to 46.0 μg/kg, while those of subsoil was in 0.74-29.7 μg/kg. The topsoil Hg content was positively correlated with TOC, with lower Hg to TOC ratio for topsoil with higher TOC. The Hg to TOC ratio of topsoil also showed significant positive correlation with atmospheric Hg deposition, modeled by the improved GEOS-Chem model on the bases of emission inventory including both anthropogenic and natural sources. Although 114 large coal-fired power plants (CFPPs), most of which were installed in recent years, were located surrounding the sampling sites in this region, they may not the main cause of increasing Hg content of topsoil in this region, because the Hg to TOC ratio of topsoil did not show significant correlation with the "power plant impact factor", which is related to the installed capacity and the distance between CFPP and the sampling site within 150 km. It may be concluded that atmospheric deposition was the main source of Hg in topsoil instead of geological sources, and power plants is not the only source of soil Hg content. Great attention on other and the potential anthropogenic sources such as residential coal combustion should also be paid for Hg emission control in this region.

MO-055

HG STORAGE AND MOBILITY IN ARCTIC TUNDRA ECOSYSTEMS OF NORTHERN ALASKA

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The main goal of this study is to constrain terrestrial Hg cycling in the arctic tundra which covers 4% of the global land surface. We present results on pool sizes and concentrations of Hg in tundra soils, vegetation, and runoff samples obtained from the northern Alaskan slope. Samples were mainly collected at Toolik Field station (68˚ 38' N, 149˚ 36' W) and along a 200km transect extending north from Toolik Field station to the Coastal Plains near Prudhoe Bay. Collected samples were analyzed for total Hg concentration, pH, bulk density, organic and total carbon, nitrogen, and major and trace elements. Runoff samples were analyzed for total Hg concentration and dissolved organic carbon. Additionally, we will present results of soil extraction experiments to assess the relevant factors related to mobility of Hg from tundra soils and transfer to aquatic systems.

Results from the Toolik Field Station show that tundra vegetation concentrations (average 112±15 μg kg-1) were 3 to 5 times higher than Hg levels generally measured at many temperate sites and are attributable to a high representation of lichen and mosses in bulk vegetation. Tundra soil Hg concentrations were 151±7 μg kg-1 in organic soils and 98±6 μg kg-1 in mineral soils, and much higher than the range of 20-50 μg kg-1 reported from upper soils in temperate areas. Permafrost soil Hg concentrations were lower than upper soils (average 40±0.2 μg kg-1) and methyl-Hg was generally 3% of total Hg. Vertical concentration patterns were relatively constant, in contrast to temperate sites showing strong declines with depth that follow the distribution of organic carbon. Mass calculations show that Hg mass in the upper 40-100 cm of the soil profile (200-500 g ha-1) was primarily stored in mineral soil layers (over 90%). Hg mass showed substantial spatial variability, particularly along an upland-wetland gradient where wetland Hg pools were much lower due to an absence of mineral soil layer. Average Hg concentrations in runoff were relatively low (4±0.4 ng L-1).

Principle component analyses including major and trace elements showed that soil Hg in surface organic layers was largely unassociated with geogenic soil elements indicating that surface soil Hg was not of lithogenic origin but derived from atmospheric sources. C-14 age-dating of deeper, mineral soil layers (14C age: 7,307 years) suggested that high concentrations of Hg present in these layers may be caused by a long legacy of atmospheric deposition and retention in soils.

MO-056

INTEGRATION OF HG FATE AND TRANSPORT IN WATERSHED TO SWAT (SOIL AND WATER ASSESSMENT TOOL)

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Computational algorithms for simulating terrestrial and aquatic biogeochemical processes of Hg were developed for simulation in the Soil and Water Assessment Tool (SWAT), a watershed scale hydrologic model developed by U.S. Department of Agriculture. The SWAT-Hg model integrates wet/dry deposited Hg species into the watershed hydrological system and estimates the transport and fate of Hg in the landscape and through stream network. The output can be used to predict the Hg levels in the fish tissue in response to climate change and variability in atmospheric mercury deposition rates. The SWAT-Hg considers three Hg species, Hg(II), Hg(0) and MeHg, in various domains of a watershed such as soils, water bodies, and vegetation. Atmospheric Hg is deposited on leaf, surficial soils (litter), or snow pack, depending on the condition of the land cover. The accumulated Hg on leaf can be washed off to surficial soil via through fall or litter fall and the Hg on snow pack can leach into soil via snow melting. After Hg partitioning between dissolved and solid phase, dissolved Hg can percolate to deeper soils, such as organic, mineral soil, and to aquifer, and can be further transported to surface water by lateral flow and return flow. Solid phase Hg in surficial soil can be released to surface water by soil erosion. In each domain, mercury can be transformed to each other via various biogeochemical reactions, such as reduction/oxidation, methylation/demthylation, and etc. These complex mercury transport and transformation behaviors are simulated in HRUs (hydrologic response units). The integration of individual Hg species behaviors in HRUs provides the Hg fate and transport in a watershed. The newly developed SWAT-Hg was calibrated and validated in the Jangsung Dam (JSD) watershed which is a headwater subbasin of the Youngsan River basin located in the south-western end of the Korean peninsula. The watershed covers a 105 km2 area, mostly pristine forests, draining into Jangsung Dam. The dam has storage capacity of 8,480 tons. The SWAT-Hg has been calibrated and validated with the data obtained in the watershed and is being applied to simulate fish mercury levels in response to environmental perturbations. The updated SWAT-Hg can be applied to other watersheds and countries to study the Hg fate and transport, because of the proven robustness of SWAT applicability to various geophysical settings.

2f-2: Mercury methylation: microbial and geochemical constraints

MO-057

METHYLATION OF INORGANIC HG CAN OCCUR IN OXIC PORTION OF OCEAN'S WATER COLUMN IN COINCIDENCE WITH PRESENCE OF ANAEROBIC BACTERIA

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In surface oceans, the euphotic zone harbors phytoplankton who facilitate oxic environment and who serve as the entry point of methylmercury (MeHg) to pelagic food webs. Production of MeHg in ocean's oxygenated euphotic zone could provide a source of new MeHg, readily available for phytoplankton uptake. Recent research points to the possibility of MeHg formation in oxic layer in the ocean and in lakes. Thus far, the mechanisms of this formation have not been identified. 2013 publication of the hgcAB gene cluster involved in methylation of inorganic Hg in sulfate reducing bacteria (SRB) has enabled searches for these genes in prokaryotic microorganisms from diverse environments. In fact, Hg methylating genes appear as rather ubiquitous and have been found in diverse environments, except for the oxic seawater. Other pathway(s) of MeHg formation in the oxic layer in the ocean have been speculated about. We argue that Hg methylation is possible in oxic seawater and that the anaerobic microorganisms could mediate this process. This argument relies on a well-supported assumption that anaerobic microorganism thrive in microscopic zones of anoxia persisting within particle aggregates. To support our hypothesis we have collected seawater from nearshore and offshore of the Eastern Long Island Sound from 2 and 18 m below surface, respectively. Particle aggregates (>300 micormeters) were settled out of the water in the laboratory immediately upon the return from the field. Aggregate DNA was extracted, preserved at -80°C and later processed by Illumina, a platform designed for high-throughput next generation sequencing. Metagenomic analysis has revealed several prokaryotic microorganisms equipped with hgcAB genes, including novel bacteria related to Desulfotignum and Desulfovibrio genera, within these settled aggregates. Moreover, unfiltered seawater was incubated at room temperature with 200Hg(II) and Me199Hg tracers for up to 24 hours to determine the rates of MeHg formation and degradation. MeHg daily rates of production were found to range from 0.1 to 0.3% and of degradation from 9 to 100%. 16S rRNA sequencing of aggregates sampled around the year from coastal Long Island Sound revealed persistence of SRB, Desulfobacterales order, identified in previous studies as capable of Hg methylation. Whereas seasonal abundance and composition of aggregates-associated SRB species shift, we suggest that Hg methylation has the potential to occur in microscopic zones of anoxia within organic matter rich particles suspended in oxic waters.

MO-058

MERCURY METHYLATION IN SETTLING PARTICLES IN THE OXIC WATER COLUMN OF A LACUSTRINE ENVIRONMENT (LAKE GENEVA, SWITZERLAND)

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Methylmercury (MeHg) formation has been shown for decades to be a process that occurs in anoxic environments. The methylation of inorganic mercury (IHg) into the hazardous neurotoxin is carried out by anaerobic microorganisms such as sulfate-reducing bacteria (SRB), iron-reducing bacteria (IRB), and methanogens. However, it has been recently demonstrated that IHg methylation occurs in particulate organic matter of the oxic water column in marine environments, and in the anoxic hypolimnion of freshwater bodies. We thus hypothesized that MeHg can also be formed in settling particles of oxic water column of freshwater ecosytems.

In this work, we measured total mercury (THg) and MeHg concentrations in settling particles and sediments collected during two years on a monthly basis from the largest oxic freshwater lake in Western Europe (Lake Geneva). THg concentrations ranged between 174 and 270 ngg-1 in sediments and from 73.4 to 257 ng g-1 in settling particles. In contrast, MeHg concentrations were significantly higher in settling particles than in sediments, ranging from 0.62 to 11.38 ng g-1 and from 0.31 to 1.67 ng g-1, respectively. Hg methylation rate constants (km) measured by species-specific isotope dilution were about 10-fold higher in settling particles than in sediments and ranged between 3.0 and 12.7 % by day. MeHg demethylation rate constants (kd) were similar in settling particles than in sediments. Accordingly, net MeHg formation increased over summer and was one order of magnitude higher in settling particles than in sediments. For a better understanding of mechanisms driving MeHg formation in settling particles of oxic water column, we amended setting particles with MoO42-, a specific inhibitor of the sulfate-reducing metabolism. Molybdate amendments reduced by 80% Hg-methylation rates in sediments and between 60% and 90% in settling particles. Moreover, positive correlation between Hg methylation rates and sulfate consumption was observed, indicating that sulphate-reduction, typically occurring in oxygen depleted zones, is an important pathway involved in MeHg in oxic lake water columns. In addition, the 16S rRNA gene was sequenced to gain insight in the biodiversity of the bacterial community and showed significant differences in abundance and richness of bacteria between settling particles and surface sediments.

This study conclusively demonstrated that MeHg can be formed within the lake oxic water column of freshwater systems, showed the role of SRB in the process, and pointed to the availability of algal-derived organic as the main driver of the process. We suggest that the contribution of this process has so far been underestimated.

MO-059

MERCURY GENOMICS IN THE ARCTIC OCEAN

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Methyl-mercury production in the ocean is likely dependent on microbial activity, however, methylation pathways remain elusive. In the Arctic, high concentrations of methyl-mercury are found in top predator marine mammals and seabirds. As a result of seafood consumption, pregnant women and women of child-bearing age in the Arctic often have blood Hg concentrations that exceed U.S. and Canadian safety guidelines. To understand the chemical cycling of mercury in the Arctic Ocean we participated in the 2015 U.S. GEOTRACES Arctic expedition (GN01) to measure Hg speciation in the water column of the Bering Sea, Makarov basin, and Canada basin between Dutch Harbor, Alaska and the North Pole. At select stations, seawater was filtered through 0.22 µm Sterivex filters and genomic DNA was collected using a phenol-chloroform extraction. Broad-range degenerate PCR primers were used to detect the presence of hgcAB, a gene cluster associated with Hg methylation, and merA, a gene that encodes for a mercuric reductase enzyme. Clade specific degenerate quantitative PCR primers were used to determine the abundance of hgcA where the hgcAB gene cluster was found. Finally, sequencing was used to identify microbial populations at depths where hgcAB and merA were detected.

MO-060

VALIDATION OF COST-EFFECTIVE MOLECULAR PROBES TO ASSESS MERCURY METHYLATION IN THE ENVIRONMENT: AN EFFORT TO LINK HGCA ABUNDANCE TO METHYL- AND TOTAL MERCURY CONCENTRATIONS

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Methylmercury (MeHg) is a common toxic contaminant in many ecosystems but the relationship between the microorganism that produce MeHg and its concentration in the environment is poorly understood. Two genes, hgcA and hgcB, are essential for microbial mercury (Hg) methylation. Detection and estimation of their abundance, in conjunction with Hg concentration, bioavailability, and biogeochemistry, are critical in determining potential hot spots of MeHg generation in at-risk environments. Equally important is the utilization of valid methods for quantifying the diversity and abundance of hgcAB. We recently developed universal qualitative PCR probes for hgcAB as well as quantitative probes that select for hgcA+ organisms from the three dominant Hg-methylating clades: Deltaproteobacteria, Firmicutes, and methanogenic Archaea. While the latter were validated using pure cultures from ~30 Hg-methylating microorganisms and environmental samples, assay sensitivity varied among species based on sequence conservation.

In an effort to link hgcAB abundance and diversity with MeHg concentrations, we used sediments from eight diverse locations and compared hgcA abundance and diversity from hgcAB PCR and hgcA quantitative PCR to 16S rRNA sequencing directly from the samples and after clone library constructions as well as to metagenomic shotgun sequencing. Currently, metagenome sequencing is regarded as the gold standard since every gene in the sample is sequenced and gene counts would yield gene abundance. The sites studied included Hg contaminated creek sediments from Oak Ridge, TN, tidal marsh samples from a Chesapeake Bay sub-estuary, MA, and permafrost from the Seward Peninsula, AK. These samples possessed Hg and MeHg concentrations over a broad range so as to encompass concentrations most likely to be observed in nature (total Hg; 0.03-14 mg Hg/kg soil) and MeHg (0.05-27 µg Hg/kg soil). The Deltaproteobacteria dominated in both metagenome and amplicon sequencing of hgcAB diversity. The data collected from 16S pyrosequencing did not identify hgcAB microorganisms well. Furthermore, qPCR estimates of Hg-methylator abundance agreed well with metagenomics estimates and displayed similar correlations with sediment HgT and MeHg concentrations.

Therefore, our PCR-based methods using hgcAB for Hg-methylator diversity and abundance is a valid means to study the relationship between Hg methylators and soil Hg concentrations. This more cost-effective and simpler approach as compared to metagenomics, will allow for more widespread use among laboratories. Utilization of this validated technique could be performed on-site or at mobile laboratories to provide rapid and accurate estimates of Hg-methylator abundance thereby quickly informing risk assessment and management as well as for remediation strategies.

MO-061

DETERMINING THE NATIVE FUNCTION OF THE MERCURY-METHYLATING GENES HGCAB: WHAT DO THEY DO WHEN MERCURY ISN'T AROUND?

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The recently described gene pair, hgcAB, is predictive for the ability of an organism to methylate mercury (Hg). The abundance of this gene pair in microbial communities where Hg is limiting, and the widespread diversity of hgcAB, suggests that this gene pair may code for an enzyme with a native physiological function beyond Hg-methylation. The hgcA gene was originally annotated as a carbon monoxide dehydrogenase (CODH) in Desulfovibrio desulfuricans strain ND132 but has a high sequence homology to the corrinoid iron-sulfur protein (CFeSP). These proteins act as methyl group carriers to facilitate the generation of acetyl-CoA in some anaerobic bacteria as part of the Wood-Ljungdahl carbon fixation pathway for acetate production. A similar action is performed by the methionine synthase, converting homocysteine to methionine. These activities both use single carbon molecules in the form of a methyl group and so such a mechanism for Hg-methylation is plausible, particularly since chloroform inhibits both CODH activity and Hg-methylation. Taken together, we hypothesize that hgcAB codes for a membrane protein complex involved in single-carbon metabolism; specifically the formation of acetate from CO2 for biosynthesis. We assayed organic acid metabolite and amino acid production from the model Hg-methylating bacterium D. desulfuricans ND132 wild-type, a mutant with the genes deleted (ΔhgcAB) and a compliment where the genes were re-introduced into the genome (ΔhgcAB::hgcAB). All cultures were batch grown in triplicate. Using pyruvate as the carbon and electron donor and fumarate as acceptor no differences in growth or CO2 production were observed but acetate production was ~1/3 of wild type yields in ΔhgcAB. With either H2/CO2 or formate the carbon and electron donor and sulfate as the acceptor, growth and acetate production was far less robust in ΔhgcAB, but amendment with acetate restored growth to wild type levels. In the pyruvate/fumarate cultures, ΔhgcAB produced 0.90 ± 0.08 mmoles acetate which is consistent with acetate production from a single decarboxylation of pyruvate. Conversely, ND132 and ΔhgcAB::hgcAB cultures produced 2.25 ± 0.07 and 2.09 ± 0.10 mmoles acetate, respectively which is not consistent with acetate production solely from pyruvate decarboxylation. Taken together, these observations support a role for HgcAB in the C1 metabolic cycle of D. desulfuricans ND132 for acetate production from several carbon sources and perhaps for methionine production and/or regulation.

MO-062

BIOGEOCHEMICAL FACTORS REGULATING MERCURY CYCLING IN BERRY'S CREEK STUDY AREA, NEW JERSEY

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Berrys Creek is a tidal tributary of the Hackensack River with a long history of human impacts. PCBs and mercury (Hg) have been identified as primary contaminants of interest. The Berrys Creek watershed includes approximately 750 acres of Phragmites-dominated marshland in a highly industrialized area, and is currently the focus of remedial investigation by a group of private companies and public agencies under the purview of USEPA. As part of this process, a conceptual biogeochemical framework was developed to provide a basis for understanding Hg bioavailability, comparing exposure risks in different parts of the Berrys Creek system, and ultimately informing decisions on appropriate remedial action.

A biogeochemical conceptual model was developed to account for key aspects of Hg partitioning (aqueous speciation, precipitation of mercuric sulfide, and binding to organic matter), and methylmercury (MeHg) formation, demethylation, and partitioning (net accumulation) to sediment. A thermodynamic reaction path model was constructed based on the conceptual model to simulate and explore relationships between total Hg and MeHg concentrations over a range of sediment conditions. Theoretical upper limiting values for MeHg concentrations in sediment are predicted by the model as a function of total Hg load and inorganic Hg partitioning mechanisms (sorption versus solubility controlled) in sediment. The universal nature of the theoretical upper limiting MeHg levels was confirmed by comparison of model predictions with an extensive compilation of site-specific data for sediments covering a wide range of Hg concentrations and environments from freshwater to marine. Sequential extraction analysis and XANES spectroscopy were also used to directly determine Hg availability and solid-phase speciation in Berrys Creek marsh and waterway sediments.

Theoretical maximum MeHg concentrations in sediments are largely a function of inorganic mercury partitioning mechanisms, which are dominated by sorption to organic matter at concentrations below approximately 1 mg/kg total mercury, and shift to a combination of sorption and precipitation of HgS at higher total mercury concentrations. The latter regime is characteristic of most of the Berrys Creek system, and XANES and sequential extraction data confirm the widespread occurrence of HgS in the form of metacinnabar in sediments. Measured MeHg levels in Berrys Creek sediments are commonly 2 to 3 orders of magnitude lower than the theoretical upper limit values, revealing the essential role of demethylation processes in limiting net MeHg accumulation within sediments. Lower MeHg levels correlate with oxic or suboxic redox regimes buffered by manganese(IV) oxides. The biogeochemical model provides a quantitative theoretically grounded framework for interpreting relationships between total Hg and MeHg levels, and understanding factors regulating Hg and MeHg cycling and bioavailability in Berrys Creek. This understanding has important implications for risk assessment and the consideration of remedial alternatives.

MO-063

SEASONAL CHANGES IN THE ROLE OF METHANOGENIC AND SULFATE REDUCING BACTERIA IN NET METHYLMERCURY PRODUCTION

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Mercury methylation is a key process in understanding the biogeochemical cycle of Hg, mainly attributed to sulfate-reducing bacteria (SRB) and methanogenic archeas . However, environmental regulation on these groups has not yet been ascertained in tropical environments, specially in respect to the flood pulse. This work aims to evaluate the variation of the net MeHg production potential in relation to biological characteristics of the periphyton, environmental characteristics, phases of the flood pulse, and how these attributes may affect the bacterial formation of methylmercury (MeHg) in a tropical wetland (Guapor River, Amazonia, Brazil). We tested net mercury methylation potentials in incubations with local water and Eichhornia crassipes periphyton/rhizomes complexes, using 203HgCl2 as tracer. Physical, biological and chemical data of the water were collected and incubations batteries with specific metabolic (algae and bacterial groups) inhibitors were performed. Our results point to a seasonal change between metabolic groups as major Hg methylators, SRB in the dry period and methanogenic archeas during the flood period. This apparent regulation can be understood by the alteration of water chemistry between flood pulse periods, mainly by sulphate compounds, and by changes in the periphytic algae composition and production. There is a positive relationship between DOC, phosphorus, cyanobacteria biovolume and methylation rates in the periphyton. These results shed new light on the plasticity of MeHg production mediated by the flood pulse in tropical flood areas as well as on ecological relationships within the periphyton.

MO-064

UNDERSTANDING THE MERCURY TRANSFORMATIONS IN SULFATE-REDUCING BACTERIAL CELLS

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Sulfate-reducing bacteria (SRB) play a key role in methylmercury (MeHg) production, which depends on bacterial strain (physiology and biomass) and on physical-chemical conditions (chemical environment of the cell). Hg behavior in cells is little known because of the difficulty in measuring intracellular Hg. In this study, we used a combination of techniques to clarify location and speciation of mercury during methylation at cellular level and at various concentrations of inorganic mercury (IHg) exposure, in order to better understand the mercury methylation process. We investigated MeHg production, IHg and MeHg distribution in cell cultures by Gaz Chromatography-ICP-MS, cell mercury location by synchrotron X-ray nano-fluorescence (nano-XRF) and transmission electron microscopy combined to X analysis (TEM-EDX), and Hg species by High Resolution X-ray Absorption-Near-Edge-Structure spectroscopy at Hg LIII-edge (HR-XANES).

Two SRB were compared, a mercury methylating *Desulfovibrio* sp. BerOc1 strain and a non-methylating strain (*D. desulfuricans* G200). Bacterial cultures growing in fumarate medium were spiked at exponential growth phase with 0.5, 5 and 50micromolar HgCl2 and incubated up to 24h. While lower IHg concentrations did not affect bacterial growth, 50micromolar completely inhibited it and represented a killed control.

3b: Rice and other foods as sources of methylmercury exposure to humans

MO-065

QUANTIFYING PRESENT AND FUTURE ATMOSPHERIC MERCURY DEPOSITION AND FATE TO RICE IN CHINA

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Consuming methylmercury (MeHg) contaminated rice is a more important MeHg exposure pathway to certain Chinese populations compared to exposure from fish. However, little is known about the sources and biogeochemical processes governing rice MeHg levels. We use modeling approaches to 1) identify locations in China where atmospheric mercury deposition to rice paddies are high, 2) understand biogeochemical processes governing MeHg sources and fate to rice, and 3) project future changes in rice MeHg levels in response to actions that implement the Minamata Convention on Mercury. We use GEOS-Chem, a global atmospheric-chemistry-transport model, to simulate present and future anthropogenic mercury emissions and deposition to China rice paddies. Future emission scenarios are implemented based on technologies and policies consistent with the Minamata Convention to regulate mercury emissions from Chinese coal-fired power plants. A rice paddy box model (flooded water, porewater, topsoil, subsoil, rice) is constructed to simulate sources, biogeochemical processes, and fate of inorganic mercury (IHg) and MeHg. Model simulations of present day atmospheric mercury deposition show that the locations where atmospheric mercury deposition to rice paddies are high are prevalent in central China (Anhui, Chongqing, Hunan, Hubei, Jiangxi). These regions demonstrate the highest rice production, consumption, and average rice total mercury concentration (49 ng/g) those that exceed the China national limit (20 ng/g). Using GEOS-Chem simulated atmospheric mercury deposition and irrigation as input, the box model adequately reproduces average China IHg and MeHg levels in the rice paddy reservoirs. Using the box model, we find that infiltration of atmospheric mercury and desorption of soil mercury into porewater are the most important processes governing the relative contribution of atmospheric mercury to rice. Sensitivity simulations show that rice IHg and MeHg levels are more sensitive to changes in infiltration, rice root absorption, and methylation compared to direct atmospheric deposition, suggesting that atmospheric deposition alone cannot explain the observed spatial variability in rice mercury levels across China. For MeHg, we estimate that a 10% change in methylation rate leads to a 9% change in rice MeHg levels. Using the future atmospheric mercury deposition scenarios, we estimate that rice MeHg levels can increase as much as 24% and decrease as much as 17% under absence and presence of stringent policy to regulate mercury emissions from Chinese coal-fired power plants, respectively. By combining these scientific measures, our future work will evaluate the present and future public health and socioeconomic costs of rice MeHg contamination in China.

MO-066

METHYLMERCURY (MEHG) IN RICE-BASED INFANT CEREALS

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Consumption of marine and freshwater fish and shellfish has long been regarded as the major pathway of human exposure to methylmercury (MeHg), as MeHg can be bioaccumulated along the aquatic food chain and elevated levels of MeHg may be present in fish and shellfish. However, recent studies have suggested that rice may contain considerable levels of mercury (Hg) including MeHg and that rice consumption could another pathway for human to be exposed to MeHg in some areas where fish consumption is limited, e.g., in Hg mining mountain areas and in certain inland areas. The occurrence of elevated levels of MeHg in rice may suggest that rice products, such as infant rice cereals, could contain the MeHg being transferred from the rice used during manufacture processes, resulting in rice cereals acting as a potential pathway of infant exposure to MeHg. In this study, more than one hundred samples of common brand infant cereals marketed in the United States and China were sampled and analyzed for the concentrations of total mercury (THg) and MeHg using cold vapor atomic fluorescence spectrometry (CVAFS) and gas chromatography (GC) coupled to AFS, respectively. The concentrations of THg and MeHg in the cereal samples ranged from 0.35 to 15.9 ng/g and from 0.07 to 13.9 ng/g, respectively, with the means being 2.86 ng/g for THg and 1.61 ng/g for MeHg. Comparisons between rice-based and non-rice cereals revealed that THg and MeHg concentrations in rice cereal samples were significantly higher than those in non-rice cereals. The results suggest that rice-based infant cereals do contain considerable levels of MeHg and rice is the primary source of MeHg in the cereals. The bioaccessibility of MeHg in the rice cereals was preliminarily assessed using physiologically based extraction methods and the potential exposure of infants to MeHg through consumption of rice cereals was evaluated. More studies are warranted to address the potential health risks of infant diet MeHg exposure through rice cereals and the regulatory implications on MeHg levels in infant rice products.

MO-067

ESTIMATING HUMAN EXPOSURE TO MERCURY THROUGH U.S. FRESHWATER FISH CONSUMPTION BY APPLYING PROBABILITY-BASED SURVEYS

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The U.S. Environmental Protection Agency (EPA) has conducted a series of national and regional screening-level studies of freshwater fish contamination since 1998. The studies are unique in that sampling locations are selected according to an unequal probability (random) sampling design, affording the first opportunity to develop statistically representative estimates of contaminants in U.S. fish relative to human health. The objectives of the probability-based studies are to: a) estimate the national distribution of selected persistent, bioaccumulative, and toxic (PBT) chemicals in fish from lakes and rivers in the conterminous U.S. and from U.S. nearshore waters of the Great Lakes; b) estimate the percentage of the sampled population of waters with contaminant concentrations above human health protection thresholds; and c) define national baselines for tracking temporal changes in PBT chemical concentrations in freshwater fish. Mercury is included as a PBT chemical because mercury fish consumption advisories are widespread in the U.S. EPA conducted the first national probabilistic study of freshwater fish contamination, i.e., the National Lake Fish Tissue Study, in 2000-2003. In 2008-2009 and again in 2013-2014, EPA conducted a comprehensive national characterization of river fish contamination during the Agencys National Rivers and Streams Assessment (NRSA). The Great Lakes Human Health Fish Tissue Study was included as a component of EPAs National Coastal Condition Assessments in 2010 and 2015.

Fillets from common sport fish species were prepared as composite samples and analyzed for total mercury, based on the conservative assumption that most mercury is present in fish fillets as methylmercury. Mercury was detected at quantifiable levels in every fish sample collected for each study. The mean weighted mercury concentrations in fish fillets from U.S. lakes in 2000-2003, rivers in 2008-2009, rivers in 2013-2014, and from the nearshore Great Lakes in 2010 were 352, 229, 230, and 171 ppb, respectively. Nearly 49% of the sampled population representing 76,559 lakes; 25-26% of the sampled population for the rivers studies (representing 51,663 river miles for the 2008-2009 study and 44,338 river miles for the 2013-2014 study); and 11% of the nearshore Great Lakes sampled population representing 4,282 square miles exceeded EPAs 300 ppb tissue-based water quality criterion for methylmercury. These exceedances indicate that the potential risk of human health impacts due to mercury exposure from fish consumption varies by waterbody type.

MO-068

EFFECTS OF HUMAN ACTIVITIES ON THE RISK OF HG IN SOIL-RICE

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Developing indicators for human exposure to methylmercury (MeHg) is critical in assessing health risk of MeHg. A number of indicators, including hair, blood, urine, and nail, have been commonly used to assess human exposure to MeHg during short (e.g., days) or mid-term (e.g., months) period, while indicators for long-term (e.g., years) exposure to MeHg are generally lacking. Here, we tried to validate a new indictor, i.e., dermal tissue, to assess long-term dietary exposure to MeHg. The validity of the indicator was examined by correlating MeHg levels in tissue samples collected from a hospital and dietary exposure to MeHg in Nanjing, a typical city in eastern China. Dietary exposure to MeHg was assessed by questionnaire survey (to obtain ingestion rates for fish and rice, the two principle dietary sources of MeHg for Chinese), determination of MeHg levels in fish and rice in Nanjing, and quantification of MeHg bioaccessibilities in cooked food samples. Meanwhile, relative contributions of fish and rice to Nanjing residents were assessed: in addition to fish, rice could contribute significantly to dietary exposure to MeHg for Nanjing residents. The indicator validated in this study would help indicate long-term dietary exposure to MeHg, and especially identify sources of MeHg exposure for human beings.

MO-069

METHYLMERCURY EXPOSURE IN CHINA

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Human exposure to methylmercury (MeHg) is often attributed to the consumption of fish. However, in our recent studies, rice, rather than fish, has been identified to be the primary pathway (>90%) for methylmercury exposure for local population in Guizhou Province, Southeastern China. Since then, several questions have been raised: Are the MeHg exposure pathways in other provinces/areas of China the same as in Guizhou? What is the level of exposure risk through consumption of fish and rice? Are there any age differences? Gender differences? Or urban-rural differences? and so on. To answer these questions and providing related advice and solutions to the environmental policymakers and the general public, in the present study, a comprehensive meta-analysis based on over 300 literatures has been conducted, covering >11,000 rice samples and >19,000 fish samples collected from 34 different administrative provinces/regions in China over the past decades from 1981 to 2015. Data analyses also included intake rates of rice and fish, body weights, and other related parameters for urban/rural (male/female) residents with different age spans. The preliminary conclusions are: 1) in the regions in inland areas of China, the main human exposure routes for methylmercury is rice (rather than fish), while in the coastal areas the major pathway is fish (instead of rice); 2) on the contribution rate of methylmercury exposure from rice, for the same province/region, the rural areas are generally higher than that in the cities (in contrast, on the contribution rate of methylmercury exposure from fish, rural areas are generally lower than that in cities) due to different dietary habits (no significant gender differences was observed); 3) The risk level of methyl mercury exposure in China has three significant characteristics: age differences (the younger, the greater the risk; and vice versa), regional differences (coastal higher than inland; cities higher than rural areas), and gender characteristics (male are generally higher than female); 4) The level of exposure to methyl mercury in China is generally low, but risk levels in coastal areas are significantly higher than in inland regions; especially, residents in Hongkong, Taiwan, Macao, and Hainan may face a certain health risks for methylmercury exposure through fish consumption.

MO-070

MERCURY IN CANNED TUNA COMMERCIALLY AVAILABLE IN CARTAGENA, COLOMBIA

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Mercury (Hg) is a complex and multifaceted pollutant. Its presence in tuna as a result of bioaccumulation, transformation and biomagnification processes is ubiquitous. As international and local agencies have done efforts to address Hg contamination, and have provided concentrations limits for this metal, countries should guarantee canned tuna available in markets may respect the regulations. In Colombia there are few studies assessing the current situation regarding Hg content in canned tuna, which is widely consumed. The objective of this research was to assess total mercury (T-Hg) levels in selected brands of canned tuna marketed in Cartagena, Colombia, determining fish consumption-based risks for ingestion. For that purpose, 252 cans of tuna were collected, representing six brands (A-F) in two mediums (water and oil). The overall mean T-Hg levels for all samples analyzed were 0.66±0.05 and 0.61±0.05 ppm, fresh weight, for water and oil, respectively. High T-Hg concentrations were detected in brands B and D. Only brands E and F offer guarantee of low risk for Hg-related health problems, as their T-Hg level was below the detection limit (0.001 ppm). According to the Colombia's Maximum Permitted Mercury Level in tuna (1.0 ppm), 15.5% of the samples exceeded this concentration, and 18.3% were greater than those recommended by the joint Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) (0.5 ppm). This work is the first to estimate the risk of eating canned tuna marketed in Cartagena city, and confirms the potential health effects to the general population; particularly vulnerable groups, such as children, pregnant women and people with heart-related problems. Government agencies should carry out tighter controls in the industry before the products hit the market, as well as random monitoring campaigns in retail chains, as a guarantee to protect human health from Hg exposure.

MO-071

MERCURY CONTAMINATION OF LARGEMOUTH BASS IN THE SOUTHEASTERN UNITED STATES

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Mercury (Hg) is a toxic metal that is found in aquatic food webs and is hazardous to human health. Consumption of methyl mercury (MeHg)-contaminated fish is the primary source of MeHg to humans. Methyl mercury concentrations in fish vary across the landscape and fish from most water bodies in the U.S. are not monitored for MeHg contamination. Therefore, it is critical that we develop the ability to predict regions that may have fish with high concentrations of MeHg. We examined the relationship between mercury deposition, landscape cover and average MeHg concentrations in 35.6-cm total length (TL) largemouth bass (Micropterus salmoides) in 24 USEPA Level III ecoregions located within 15 states in the southeastern U.S. (from Texas to Maryland). The National Descriptive Model of Mercury in Fish was utilized to estimate concentrations of MeHg in largemouth bass. Mercury deposition was estimated using wet Hg deposition data from the Mercury Deposition Network. To determine landscape cover, we used the National Land Cover Database. We used ecoregions as the unit of analysis because they are well-suited for spatial studies. In 20 ecoregions, the average MeHg concentrations in largemouth bass were above 300 ng/g ww, the threshold concentration of MeHg recommended by the USEPA for the issuance of fish consumption advisories. Six ecoregions had average MeHg concentrations in largemouth bass 600 ng/g. Mercury deposition adjusted for conifers and wetland coverage accounted for 76% of the variance in average MeHg concentrations in largemouth bass in ecoregions. To estimate the risk to humans, we computed the percentage of water bodies in each ecoregion with MeHg in largemouth bass above 300 ng/g ww. The percentage of water bodies increased as a sigmoid function of average MeHg in largemouth bass in ecoregions, with 13 of 24 ecoregions having 50% of the waterbodies with 35.6 cm TL largemouth bass having MeHg concentrations > 300 ng/g ww. We estimate that 58.6% of the 3 million lentic waterbodies in the southeastern U.S. may contain largemouth bass with concentrations of MeHg that are hazardous to humans. Because it is not possible to sample all water bodies in ecoregions with hazardous levels of MeHg in gamefish, we recommend county-level fish advisories be issued to warn citizens about the hazards of consuming gamefish from public and private water bodies.

MO-072

DECLINING MERCURY CONCENTRATIONS IN BLUEFIN TUNA

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Tunas are apex predators in marine food webs that accumulate mercury (Hg) to higher concentrations than most other fish. High human consumption and moderate to high species-dependent Hg concentrations cause tunas to provide more Hg (~40%) to the U.S. population than any other source. Reduced Hg emissions in North America in recent years have decreased Hg concentrations in North Atlantic waters and investigating whether changes propagate up to top predators is a key to evaluating the benefits of emission reduction efforts. To investigate recent temporal Hg trends in the largest and longest-lived tuna species, we measured total Hg concentrations in 1,292 Atlantic bluefin tuna (ABFT, Thunnus thynnus) captured in the Northwest Atlantic from 2004 to 2012. Mean Hg concentrations in ABFT muscle tissue were 0.76 ± 0.33 ppm; concentrations increased nonlinearly with length, weight, and estimated age, ranging from 0.25 ppm in fish <100 cm in length to 3.15 ppm in fish >250 cm (14-15 years old). No significant differences in Hg concentrations were noted between male and female ABFT. For six size classes of ABFT corresponding to 9-14 year old fish, the Hg concentrations declined significantly over time of capture, at a rate of 0.018 ± 0.003 ppm per year or around 2% per year. The decline rate of 19% over an 8-year period from the 1990s to the early 2000s paralleled comparable declines in anthropogenic Hg emission rates in N. America,

N. Atlantic atmospheric Hg0 concentrations, and N. Atlantic seawater concentrations during this period. Because of their pronounced migratory behavior, Hg concentrations in ABFT are presumed to reflect ocean basin-wide exposures (through forage fish) rather than local exposures at one particular location. It thus appears that reductions in atmospheric Hg loading have rapidly propagated up marine food webs to a commercially important species, suggesting that emission reduction efforts have resulted in lower Hg concentrations in large, long-lived fish.

3c-2: Risk assessment of mercury exposure to fish, birds, and wildlife

MO-073

CONTROLS ON VARIATION IN FISH HG CONCENTRATIONS IN STREAMS OF THE ADIRONDACK REGION, NEW YORK: DEVELOPMENT OF A SIMPLIFIED SCREENING APPROACH TO IDENTIFY HOT SPOTS

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Simplified screening approaches for the neurotoxin mercury (Hg) may be helpful in risk assessments of natural resources in aquatic ecosystems. We explored the development of a simple screening approach in the Adirondack region of New York, USA, a known Hg hot spot with previously demonstrated high levels of bioaccumulation. Thirty-six small, perennial streams were sampled and analyzed for major solutes and Hg concentrations in fish tissue. These streams were broadly representative of a population of 391 Adirondack streams derived from previous investigations. Data analyses were based on length-normalized site median Hg concentrations in juvenile and adult Brook Trout, Creek Chub, Blacknose Dace, and Central Mudminnow and on median multi-species z-scores. Several landscape and chemical metrics known to be strongly related to methyl Hg concentrations in aquatic biota were explored for their strength of association with fish Hg concentrations. Surprisingly, none of the landscape metrics, including percent wetland area and mean basin slope, were significantly related to regional variation in fish Hg concentrations across the 36 streams. In contrast, several chemical metrics including dissolved organic carbon (DOC) concentrations, sulfate concentrations (SO4), pH, ultra-violet absorbance at 254 nm. (UV254), and specific ultra-violet absorbance were significantly related to regional variation in fish Hg concentrations. A cluster analysis based on the chemical metrics identified three distinct groups of streams, but all three groups were significantly different only for pH and not the other measures. Further analysis combined the data into two clusters that were most self-similar for further analysis. Among these two clusters, DOC, SO4, pH, UV254, and fish z-scores were all significantly different ($p<0.05$). Screening values of DOC>6.9 mg/L, SO4<2.8 mg/L, pH<6.6, and UV254>0.31/cm were suggested as thresholds to identify Adirondack stream sites likely to have the highest fish Hg concentrations. These values were especially effective predictors of high Hg streams likely to have at least one fish species with fish Hg concentrations greater than 100 ng/g, a level of concern for fish consumption by wildlife. A projection of Hg risk based on DOC concentrations to the larger population of 391 streams showed that about 28% were likely to have high wildlife risk, and these streams were located mainly in the western part of the Adirondacks. Finally, fish Hg/DOC ratios in this data set suggest less efficient uptake of Hg as stream DOC concentrations increase, consistent with the results of several recent studies.

MO-074

CONCENTRATIONS OF METHYLMERCURY AND SELENIUM IN FISH IN NATIONAL PARKS OF THE NORTHWESTERN LAURENTIAN GREAT LAKES REGION (USA).

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Multiple studies have reported that fish in the Laurentian Great Lakes region are contaminated with elevated concentrations of methylmercury. However, little is known of concomitant levels of seleniuman element that binds with mercury and may ameliorate mercury toxicity when molar concentrations of selenium exceed those of mercury (i.e., molar ratios greater than 1.0). We measured mercury and selenium in axial muscle and liver of Northern Pike (Esox lucius), Smallmouth Bass (Micropterus dolomieu), and Largemouth Bass (Micropterus salmoides) sampled in spring 2008 2012 from lakes in Indiana Dunes National Lakeshore, Voyageurs National Park, Isle Royale National Park, Sleeping Bear Dunes National Lakeshore, and Pictured Rocks National Lakeshore. Not all species were obtained at all locations in all parks. Concentrations of mercury in axial muscle tissue of some predatory fish in all lakes exceeded the USEPA tissue residue criterion of 300 ng/g wet weight for methylmercury, a criterion established to protect the health of humans who eat noncommercial, wild fish. Selenium concentrations were negatively correlated with mercury in axial muscle of Northern Pike, but not Smallmouth or Largemouth Bass. Molar ratios of selenium to mercury ranged from 0.18 to 25, but were less than 1.0 in approximately 50% of fish with mercury concentrations greater than 300 ng/g wet weight. Concentrations of selenium and mercury in livers were positively correlated and molar ratios of selenium to mercury always exceeded 1.0, ranging from 1.8 to 85. However, there was evidence of cellular damage in livers with increasing concentrations of mercury. Lipofuscin, a pigment that accumulates in the liver of fish as a result of cell damage, can be measured spectrophotometrically and was positively correlated with liver mercury. In addition to predatory fish, prey fish were sampled in these five parks and from three streams in Grand Portage National Monument to assess the risk of methylmercury to fish-eating birds. Maximum concentrations of mercury exceeded

180 ng/g in whole body of prey fish--threshold effects levels associated with reduced reproduction in fish-eating birdsin nine of twenty-three water bodies in the six national park. Whole body molar concentrations of selenium exceeded mercury in all prey fish sampled. These results suggest that fish, humans who eat fish, and piscivorous birds are at risk from methylmercury exposure at a substantive number of locations within these parks and this risk may not be ameliorated by selenium.

MO-075

MERCURY-SELENIUM MOLAR RATIOS IN FISH ACROSS GRADIENTS OF METAL EXPOSURE IN THE WESTERN UNITED STATES

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Mercury (Hg) and selenium (Se) can threaten wildlife and impede ecosystem restoration efforts across a range of habitats. Selenium also interacts with Hg by impacting both biogeochemical processes in the environment and physiological processes within organisms. In particular, when Se in tissues is present in molar quantities that equal or exceed Hg, it may bind the methylmercury rendering it unavailable, thereby reducing its toxicity. Total Hg (THg) concentrations in fish from streams across the western United States have shown to inversely correlate with Se concentrations in tissues, with most fish having a molar THg:Se ratio <1 (excess Se), indicating that these fish may be less at risk for Hg toxicity than previously thought. Yet, the specific mechanisms controlling molar THg:Se ratios in nature are far from clear and we lack understanding of the importance of physiology, food web energetics, aquatic biogeochemistry and underlying geology in driving these ratios. We evaluated the relationships between Hg and Se concentrations in fish from across western North America to better understand the spatial variability in these relationships. Importantly, the expansive dataset compiled in this synthesis effort spans large gradients in both Hg and Se exposure, includes measurements in both muscle and whole body tissues, and includes a large number of species representing many feeding guilds. Molar Hg:Se ratios in more than 8,000 whole body fish samples ranged from 0.003 to 42 with a mean molar ratio of 0.54 (median = 0.24). Similar to prior published studies, more than 97% of the fish sampled had THg:Se molar ratios <1 (excess Se). Molar ratios in tissues varied among foraging guilds and to a lesser degree, geographical regions. Piscivores tended to have higher THg:Se molar ratios than benthivore or generalist species, possibly due to them feeding higher in the food chain where Hg biomagnifies. Mercury concentrations did not appear to influence the slope of the relationship between molar THg:Se and THg concentrations in muscle tissues when individuals were grouped into high (>1.5 µg/g dry weight) and low THg concentrations. But, a higher slope was observed between molar THg:Se ratio and THg concentrations in whole body samples (all foraging groups). Selenium excess over THg was greater in whole body samples compared to muscle tissues in all foraging groups. These results indicate that molar THg:Se ratios are affected by multiple interdependent factors that should be considered when assessing the potential protective role of Se in mitigating the toxic effects of methylmercury.

MO-076

INVESTIGATION OF MERCURY TOXICITY IN LANDLOCKED ARCTIC CHAR IN HIGH ARCTIC LAKES

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In the Canadian Arctic, mercury (Hg) concentrations in the tissues of non-anadromous (landlocked) Arctic char are elevated with ~30% of the sampled populations exceeding toxicity thresholds. In 2011, 2012, 2015, and 2016 we collected tissues (liver, muscle, brain) from Arctic char (n=227) from four lakes (Small, North, 9-Mile, and Amituk) on Cornwallis Island, Nunavut. The lakes sampled span a gradient of Hg contamination, allowing for the comparison of biological endpoints in char with low Hg concentrations to char with high Hg concentrations. The objectives of this research were to (1) measure total Hg and Hg speciation in Arctic char livers, brains and subcellular components, (2) determine correlations between Hg concentrations and biomarkers of oxidative stress in livers and brains, and (3) assess potential histological changes in livers and brains in relation to Hg exposure. Results thus far show a wide range in total Hg concentrations in Arctic char among lakes (0.04 to 2.6 parts-per-million wet weight in muscle), with about 36 % of individuals exceeding a toxicity threshold of 0.5 parts-per-million wet weight. Methylmercury was the predominate form of total Hg in liver (~80 %), where concentrations were two to three times higher than in muscle (to a maximum concentration of 6.5 parts-per-million wet weight). Total Hg was predominately found in the sensitive subcellular pools (mitochondria, microsomes and lysosomes, and heat-denatured proteins, including enzymes) of low- and high-Hg char, suggesting that increasing Hg exposure does not result in an activation of detoxification mechanisms in the liver. This may explain histological changes in the livers of fish from the most contaminated lake. Furthermore, a significant fraction of Hg may exit the liver and reach the brain, as concentrations in the two organs were similar. This research goes beyond documenting Hg concentrations in fish and will provide critical knowledge concerning fish health status.

MO-077

IMPACTS OF METHYLMERCURY BIOACCUMULATION IN MARINE FOOD WEBS ON THE HEALTH AND SUSTAINABILITY OF TUNA FISHERIES IN THE PACIFIC OCEAN

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The toxic effects of methylmercury (MeHg) on wildlife are well known, but impacts on the health and sustainability of global fisheries have not been well-characterized. Global tuna fisheries account for a large fraction of human exposure to methylmercury in many countries but are also an important food source of protein and essential nutrients for many populations. We have developed a framework for connecting our existing knowledge of mercury emissions and biogeochemistry to its impact on fisheries. In prior work, we have developed a modeling framework for simulating the global fate and transport of mercury in the atmosphere, terrestrial ecosystems and the oceans, including conversion to the bioaccumulative species methylmercury and uptake at the base of the oceanic food web. Here we link this simulation to a dynamic model of growth, reproduction and biomass of fish stocks and their interactions with the environment and fishing (Dynamic Bioclimate Envelope Model). We use a food-web bioaccumulation model to provide information on both the magnitude and timing of changes in fish MeHg levels relative to seawater. We specify dose-response relationships for methylmercury based on a review of the ecotoxicological literature on exposure impacts on growth, reproduction and body size of fish. When forced by the all-time historical emissions and future emissions scenarios developed by Argonne National Laboratory, we project a 30-50% increase from present day in seawater MeHg concentrations under business-as-usual future emissions and a 0-10% decrease under future mercury controls. Pacific tuna concentration changes show small lags (less than a decade) relative to seawater concentrations, with the lag depending on the size/age of the fish. We find that the long-term fish-specific MeHg trends are significantly affected by inter-annual variability in water temperature. We will discuss the impact of MeHg on maximum sustainable yields for fisheries of these commercially important species.

MO-078

LINKS BETWEEN MERCURY CONTENT AND SUSTAINABILITY OF FISHERIES: ECOLOGICAL EXPLANATIONS AND IMPLICATIONS

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Differences in the impacts of stressors such as mercury toxicity and overfishing among fish species are not adequately understood, but are likely to have important consequences on the quality and supply of commercial fish for human consumption. Mercury can bioaccumulate to potentially toxic levels in fish, and fishing pressure driven by global fish consumption is on a steady rise. Both factors can increase stress on wild fish populations. However, the demographic impacts of these stressors will vary across fish species due to differences in their resilience, or ability to withstand stress. Here we examine relationships between fish mercury concentrations and resilience across a broad range of fish species. We hypothesized that fish with the lowest resilience, indicated by multiple measures of population productivity, are also at greater risk of having elevated, potentially toxic mercury content due to shared, underlying relationships with larger body size, and slower growth. We combined and analyzed existing data on total mercury concentrations from the Seafood Mercury Database, and life history characteristics from Fishbase, for approximately 400 species of finfish. We found that 83 (21%) species had total mercury levels exceeding the conservative toxicity threshold of 0.5 ppm (w.w.) associated with suppressed reproduction, growth, and behavior in freshwater fish. These species were dominated by large-bodied, marine pelagics, such as tunas and sharks. Of the 83 species with elevated mercury content, 34 (42%) are currently classified as vulnerable, near threatened, threatened, endangered, or critically endangered by the IUCN. Across all species in the analysis, both mercury content and resilience were strongly, positively related to body size, length at first maturity, maximum age, and negatively related to growth rate (measured as the Von Bertalanffy rate to reach asymptotic length). Thus, large, slow growing fish species are both at higher risk of having elevated, potentially toxic mercury levels, and are less likely to recover from population decreases due to stressors in general. Future studies should examine the combined and relative risks of mercury toxicity, overfishing, and other pressures, and prioritize their relevance to large, slow growing, commercially important fish.

MO-079

LONG-TERM MONITORING AT THE FORMER PINCHI LAKE, BC MERCURY MINE – RESULTS OF THE 2016 EVENT AND RISK IMPLICATIONS FOR FISH AND WILDLIFE

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The Pinchi Lake Mercury Mine in northern British Columbia, Canada produced elemental mercury (Hg) from 1940 to 1944 (historical operation) and from 1968 to 1975 (modern operation). During historical operations, mercury-contaminated calcines (primarily as cinnabar [HgS]) were deposited directly into Pinchi Lake (55 km2). Investigations conducted over the last two decades focused on characterizing the extent and magnitude of mercury (and other contaminants) contamination and associated environmental risks on the mine site and throughout the Pinchi Lake aquatic receiving environment. Results of

these efforts informed the development of a closure plan for the upland mine site (implemented in 2010 to 2012) as well as a long-term aquatic monitoring program for Pinchi Lake. As part of continued monitoring, a comprehensive study was conducted in 2016 to document the current status of Hg in the Pinchi Lake ecosystem relative to a nearby reference lake (Tezzeron). In addition, a detailed sediment coring program was conducted, repeating a 1997 investigation, to provide updated information on natural recovery.

The 2016 results provide an updated context to the long-term monitoring data set. Pinchi Lake fish mercury concentrations remain elevated relative to nearby reference lakes and are attributable to historical mine operations, nearly 60 years earlier. Mercury concentrations in sediment cores remain high and show measurable, but slow natural recovery due to burial. While Hg/MeHg concentrations in water and zooplankton are low and similar historically and to many lakes elsewhere in Canada, they are still elevated relative to nearby Tezzeron Lake. Although fish mercury concentrations in lake trout standardized to 55 cm have declined significantly since the 1970s (~5 ppm), the trend in declining concentrations is quite slow (~1 ppm in 2016). Despite reductions in fish mercury concentrations, they are sufficiently elevated to potentially cause effects to fish and fish-eating wildlife based on literature studies. However, field investigations have not detected adverse ecological effects on fish, nor to local piscivorous birds (red-necked grebe, bald eagle) and mammals (river otter).

MO-080

A WATERSHED-LEVEL RISK-BASED APPROACH TO ADDRESS LEGACY MERCURY IN THE SOUTH RIVER (VIRGINIA, USA): BASELINE ECOLOGICAL RISK ASSESSMENT (BERA) AND ITS IMPLICATIONS

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Legacy mercury (Hg) contamination is a complex environmental challenge in river systems, requiring substantial resource to adequately understand the problem and collaboration among multiple stakeholders for a meaningful and pragmatic solution. A regulatory-driven, watershed-level baseline ecological risk assessment (BERA) for the South River (Virginia, USA) provides a unique example of the scale, complexity, and collaboration involved to address legacy Hg contamination in a river system. Mercury release to the South River occurred from a former DuPont plant between 1929 and 1950 when it was used in acetate flake and yarn production. This caused potential impacts to the aquatic and riparian terrestrial systems (including the areas within the 62-year floodplain) along approximately 25 miles of the river downstream of the former plant. Legacy Hg in the potentially impacted areas has been the subject of numerous studies over the last four decades. The South River Science Team (SRST), a multi-stakeholder collaborative program, was established in 2001 to investigate the Hg issue in the study area. The BERA integrated extensive chemical, physical, and biological data to assess the potential ecological risk and was performed as a part of the US Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI). This presentation will focus on the collaborative approach to the BERA process and the implications of the BERA results on the remedial approach.

3e-2: Human exposure and health effects of mercury: epidemiology and population studies

MO-081

TRENDS IN SPECIATED AND TOTAL BLOOD MERCURY CONCENTRATIONS IN THE U.S. POPULATION, SURVEY YEARS 2003 - 2014

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The Centers for Disease Control and Preventions Inorganic and Radiation Analytical Toxicology Laboratory measures total mercury, inorganic mercury, ethyl mercury, and methyl mercury in people age one and older in the U.S. population as part of the National Health and Nutrition Examination Survey (NHANES). Analysis of specific mercury species began in 2011 and has allowed us to determine baseline levels of inorganic, methyl, and ethyl mercury for the United States population. A number of studies have looked at either total mercury or total and inorganic mercury in specific demographic groups, but we have four years of data that looks at those forms of mercury and additional forms across several demographic groups. We evaluated all available NHANES data for total, methyl mercury, and inorganic mercury for survey years 2003 through 2014. With new data from NHANES 2013-14, we have a more comprehensive picture of the trends of mercury in the U.S population over time.

We were able to statistically evaluate the data for the 95th percentile of the population and identify the key demographic characteristics including gender, ethnicity, education and household income that have an impact on the likelihood of an individual being placed into the 95th percentile. This statistical evaluation was completed for total, inorganic, and methyl mercury to further assess the differences that exist. Beginning in survey year 2011, the survey started oversampling Asians which affords us the opportunity to provide estimates of Asians in addition to Non-Hispanic White, Non-Hispanic Black and all Hispanic race/ethnicity groups. There is a statistically significant difference in the prevalence of mercury in the Asian segment of the population that was surveyed as opposed to other ethnic groups. This correlates to dietary trends (i.e. higher fish consumption). Household income is another demographic variable in survey years 2011 through 2014 where an increase in income has led to an increase in mercury exposure, possibly through higher seafood consumption. NHANES mercury data provides a unique opportunity to evaluate mercury trends over time in a representative sampling of the U.S. population. An overview and trends of the NHANES speciated mercury results from 2003 to 2014 will be presented along with highlights of significant findings of different demographic characteristics.

MO-082

HUMAN MERCURY LEVELS IN URBAN SOUTH INDIA AND EVALUATION OF EXPOSURE PATHWAYS THROUGH STABLE ISOTOPE ANALYSIS

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India is a major consumer of coal. There are 132 coal-fired power plants (431 units) in India, which meet >51% of India's commercial energy demand. In this work, we investigated the possible role of power plants in increasing the local exposure to mercury. We also develop baseline for several demographics. A new category, oldsmiths, different to ASGM workers, is also included.

We analysed mercury in hair from 668 volunteers in three cities in South India (Hyderabad (n = 103) in interior, Vasco da Gama (n = 326) on the west coast and Nellore (n = 239) on the east coast that has 4 active coal-fired power plants). Baseline Hg levels in some demographic categories were: subsistence fishermen/women (n = 66) [Geometric Mean (GM): 0.38 µg/g (95% CI: 0.34-0.42 µg/g)], goldsmiths (n = 21) [GM: 0.22 µg/g (95% CI: 0.18-0.28 µg/g)]. Women of child-bearing age had Hg levels of (0.14 µg/g (95% CI: 0.12-0.16 µg/g), similar to US NHANES and European DEMOCOPHES studies after accounting for diet and age.

The GM of hair Hg levels of people from Nellore (n = 239) [0.19 µg/g (95% Confidence Interval (CI): 0.09-0.37 µg/g)] are statistically ($p < 0.05$) higher compared to both Vasco da Gama (n = 326) [0.13 µg/g (95% CI: 0.05-0.37 µg/g)] and Hyderabad (n = 103) [0.08 µg/g (95% CI: 0.04-0.15 µg/g)]. This was true for different fish consumption frequencies (rare, once a week, thrice a week), even though fishes consumed were from similar trophic levels. Majority of volunteers consumed rice and which was primarily locally grown. Vegetarians (who never ever consumed fish) from Nellore (n = 37) [0.09 µg/g (95% CI: 0.03-0.13 µg/g)] had higher ($p < 0.05$) GM hair Hg values compared to vegetarians from Vasco da Gama (n = 47) [0.03 µg/g (95% CI: 0.01-0.06 µg/g)]. Preliminary results indicate that rice samples from Nellore appear to have higher concentration of Hg than rice samples from other sites.

Our results suggest that exposure to mercury may be higher in Indian regions that have active mercury sources in their vicinity. Since there are more than 100 power plants in India, the implications to mercury exposure may be substantial. We are now studying mercury isotopes in hair samples from our study population to further investigate this hypothesis, and results will be presented in the conference.

MO-083

LOW MERCURY LEVELS IN HUMANS AND FISH FROM THE CIÉNAGA GRANDE DE SANTA MARTA, CARIBBEAN COAST OF COLOMBIA

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Mercury (Hg) is a heavy metal pollutant with high toxicity. It is being released into aquatic ecosystems of Colombia by gold mining activities, where it is used to extract the precious metal. One of these ecosystems is the Magdalena River, which near the Caribbean Coast, it provides freshwater to the Ciénaga Grande de Santa Marta (CGSM), the largest and most productive coastal lagoon complex in Colombia. To evaluate mercury pollution status in the CGSM, total mercury (T-Hg, fresh weight) was measured in the hair of 158 habitants from two stilt-house towns, Nueva Venecia and Buena Vista. Total Hg was also measured in the muscle and liver of several common fish species. The measurements were performed using a direct mercury analyzer, DMA-80. Low T-Hg levels were detected in hair from humans, with average concentrations of 0.71±0.04 and 0.70±0.08 ppm, for Nueva Venecia and Buena Vista, respectively. Males had greater T-Hg concentrations (0.81±0.05 ppm) than females (0.63±0.04 ppm). Occupation is also a factor that determines T-Hg in hair, with the largest average detected in fishermen (0.87±0.06 ppm), when compared to other examined groups, such as housewives or students. Low levels of T-Hg were found in fish muscle, although there were significant inter-species differences in Hg content: Cathorops mapale (0.094±0.003 ppm, n=36) > Notarius bonillai (0.083±0.001 ppm, n=2) > Megalops atlanticus (0.081±0.002 ppm, n=22) > Mugil incilis (0.079±0.003 ppm, n=34) > Elops saurus (0.078±0.003 ppm, n=17). Total Hg in liver showed not significant differences between Mugil incilis (0.082±0.004 ppm, n=13) and Megalops atlanticus (0.088±0.004 ppm, n=22). These results indicate that consumption of fish from CGSM is not resulting in Hg accumulation in humans. Therefore, the risk of developing Hg-related health problems is considered negligible. Much more important is the fact that in some places of Colombia, it is still possible to find aquatic habitats where Hg is not a concern for human health and welfare.

MO-084

MATERNAL PRENATAL BLOOD MERCURY AND OFFSPRING IQ AT 8 YEARS IN A TYPICAL UK POPULATION

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Background. World-wide current recommendations for pregnant women are to eat fish with caveats to avoid species with high levels of mercury resulting in a reduction in seafood consumption in some pregnant women. There is conflicting evidence concerning the harm from mercury in regard to offspring cognitive outcomes if the woman eats fish.

Methods. This study uses the ALSPAC study of pregnancies in 1990–92. Mercury levels were measured in whole blood in early pregnancy, and outcomes for 2062 children were the verbal, performance and total IQ measured at age 8 treated as (a) continuous and (b) as the lowest 25% of the distribution. Multiple and logistic regression analyses took account of social and demographic variables, and stratified analyses considered children of fish eaters separately.

Findings. Before adjustment, the mean IQs increased with increasing mercury (change with 1SD of mercury = +2·02; 95%CI +1·40, +2·64 IQ points); after adjustment the effect size was reduced although still positive (+0·61: -0·06, +1·29 IQ points). However when mothers who ate fish were considered separately, the adjusted positive relationship was stronger (+0·84: +0·13, +1·56 IQ points), in comparison with the outcomes for the women who did not eat fish where the adjusted relationship was negative (-2·22: -5·00, +0·56 IQ points). Results for the binary outcome showed a similar pattern with the adjusted OR for non-fish-eaters 1.79[95%CI 1.10,2.93], significantly different from that for the fish consumers [0.94; 95%CI 1.10,2.93].

Interpretation. This suggests that the relationship between intrauterine exposure to mercury is benign in regard to offspring IQ provided the mother consumed fish. On the present evidence, pregnant women should be assured that consumption of fish is likely to be more beneficial than harmful to the developing child.

MO-085

GLOBAL BURDEN OF DISEASE DUE TO MODERATE CHRONIC METALLIC MERCURY VAPOR INTOXICATION RESULTING FROM MERCURY USE IN ARTISANAL SMALL-SCALE GOLD MINING

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Background: Artisanal and small-scale gold mining (ASGM) is the major source for mercury emissions globally. Toxic mercury causes negative health effects especially for miners working directly with mercury such as panners and amalgam smelters. Good and reliable data is difficult to obtain, because ASGM activities are largely informal and take place in remote mining areas. Thus, the global burden of disease due to mercury used in ASGM is unknown.

Objective: To calculate a first rough estimate of disability-adjusted life years (DALYs) caused by chronic metallic mercury vapor intoxication (CMMVI) in miners worldwide resulting from the use of mercury in ASGM.

Methods: A primary data set was set up including all obtainable studies where data was sufficient to determine the prevalence rate of CMMVI with a diagnostic tool. Further studies reporting only mercury levels in urine were reanalyzed using the primary dataset to obtain a valid prevalence rate. The prevalence rate was multiplied with the number of miners for each country taken from a literature search which supplemented available reviews and the disability weight (DW) for moderate CMMVI. The DW contains information about the severity of the intoxication in comparison to other diseases. Mortality was ruled out as outcome. Uncertainty intervals (UI) were quantified to account for uncertainties in the input data (number of miners, DW).

Results: Concentrating on moderate CMMVI, the burden of 14 to 19 million gold miners ranges from 1.22 (UI 0.87-1.61) to 2.39 (UI 1.69-3.14) million DALYs due to moderate CMMVI. This estimate is based on human biomonitoring data from 3,194 gold miners. A number of 62 countries were taken into account of which most countries with available data belong to the African region. Subject to the quantification, nearly every fourth up to every third miner is expected to be mercury intoxicated.

Conclusions: Our results give a first rough estimate of global DALYs, based on country estimates of the use of mercury in ASGM. A major limiting factor is the limited data availability regarding human biomonitoring data, health assessments, and the number of affected miners. We estimate the disease burden of about 3.3 to 6.5 million intoxicated miners. Our results show, that ASGM is a global environmental health hazard. Further research is needed to improve the model input parameters.

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Conflict of interest: The authors declare no competing financial interests.

MO-086

MERCURY EXPOSURE BIOMARKERS DIFFER BETWEEN LICENSED AND UN-LICENSED ASGM MINERS IN TARKWA, GHANA

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Workers within artisanal and small-scale gold mining (ASGM) communities are amongst the highest Hg-exposed groups worldwide. While formalization of this sector has been suggested as a means to reduce exposures and improve health and safety, we are unaware of empirical evidence that supports this notion. The objective of this study was to compare mercury exposure profiles among miners working in licensed versus un-licensed ASGM sites. To achieve this, 404 small-scale miners were recruited in 2014 from 9 mining sites in Tarkwa (Ghana), of which 5 were licensed and 4 were not licensed. Miners were interviewed, and urine and hair samples were taken for measurements of total Hg content in a subset (n=316). Sociodemographic characteristics of miners from the two groups were relatively similar (33.8 yrs old, 92% male, 29% completed high school, 66% living with a partner). Those currently working in an un-licensed mine have higher mean levels of total Hg in urine (110.7 vs 16.0 ug/L; $p<0.001$) and hair (4.5 vs. 2.0 ug/g; $p=0.09$) compared to workers from the licensed mines. A range of other information was collected showing differences between these groups of miners such as work history and injury episodes, and these will be discussed. These findings advance our understanding of mercury exposure (and other differences) amongst ASGM workers especially important differences between miners working in a licensed versus and un-licensed site.

MO-087

MERCURY ENVIRONMENTAL AND HUMAN HEALTH RISK ASSESSMENT PROVIDES SCIENCE BASE FOR PERU'S STATE OF EMERGENCY IN MADRE DE DIOS

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In May 2016, the Peruvian Ministry of Health (MINSA) declared a State of Emergency due to high mercury levels reported in Madre de Dios (MDD), Peru. This declaration stemmed from three interrelated projects studying the impacts of road construction, gold mining, and gas extraction on human and environmental health that recorded elevated mercury levels in human and environmental samples. Here, study designs, exposure assessments, and preliminary findings associated health outcomes to mercury exposure are reported. The studies include: (1) Interoceanic Highway Study (IOH); (2) Rio MDD Study (RIO); and (3) Amarkaeri Cohort Study (AmCS). The IOH and RIO studies were population-based samples (a 2-stage selection design and a stratified sampling design, respectively), while the AmCS was a census of rural communities and a 50-75% sample of three peri-urban communities all surrounding the Amarakaeri Reserve. Total mercury contents in hair were evaluated in all household members for the IOH and RIO studies, but only in sentinel groups for the AmCS (women of child-bearing age, their children and spouse). In total, hair mercury was evaluated in 724, 231, and 2308 persons from the IOH, RIO and AmCS, respectively. Among all samples, median mercury levels were high (1.47 ug/g, IQR: 0.71-3.01), with 57.5% and 39.2% exceeding the USEPA (1.2ug/g) and PERU/WHO (2.0 ug/g) exposure thresholds, respectively. High hair mercury was correlated with increased fish consumption in RIO participants, particularly high trophic level fish, negatively correlated with quinoa and kiwicha consumption (Wyatt et.al in-review). Spatial interpolation of mercury levels identified the highest exposures in communities 90-120 km upstream of ASGM (n=216), where 96.8% and 90.7% exceeded the USEPA and PERU/WHO guidelines (20% exceeded 9.0 ug/g). In addition, fish, sediment, and water were obtained from river sections near, upstream and downstream of ASGM (Diringer et.al 2015): The highest total Hg in fish and total Hg and methylmercury in sediments were observed within and downstream from ASGM concession areas. River sites upstream of mining did not have high Hg in sediment or fish. These two findingslow environmental mercury, but high human exposureare in direct contrast that may be due to river transport of Hg-containing sediment, behavioral differences in diet, or ecosystem services affecting methylation.Preliminary analyses evaluating health impacts suggest significant associations between mercury levels and mitochondrial DNA copy number (RIO), anemia risk (AmCS), impaired neurocognitive function in children (AmCS) and impaired kidney function (AmCS).

MO-088

CHARACTERISTICS AND INFLUENCING FACTORS OF INHABITANTS DUE TO MERCURY EXPOSURE IN THE SMELTING AREA, NORTHEAST OF CHINA

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The aim of this work was to study mercury accumulation in inhabitants from smelting area, and their health risk due to mercury exposure. The investigation included the: (a) distributions of Hg in diet, dust and water, (b) mercury accumulation and influencing factors in hair and blood of inhabitants, and (c) assessment of health risks due to mercury exposure. Smelting activities from Huludao zinc plant in Liaoning province, northeast China had seriously contaminated the surrounding environment. In the smelting district of Huludao, THg contents of the seeds of maize, soybean, and broomcorn are 0.008, 0.006, and 0.057 mg/kg, respectively, exceeding the maximum level of contaminant in food (GB2762-2005) by 4.7 times. The edible parts of vegetables are also contaminated with a range of mercury contents of 0.001–0.147 mg/kg (dry weight). The average and maximum mercury daily intake (DI) of adult around the Huludao zinc plant via consuming vegetables are 0.015 and 0.051 lg/kg/d, respectively, and those of children are 0.02 and 0.07 lg/kg/d, respectively. The average and maximum weekly intakes of total mercury for adult are 2.1 and 7.1%, respectively, of the provisional tolerable weekly intake (PTWI), and 2.8 and 9.7%, respectively, of the PTWI for children. The maximum Hg, contents in dust were 5.324 mg/kg, and were 144 times as high as the background values in soil. Children were also experiencing the potential health risk from Cd and Pb exposure from dust near HZP, not include Hg. The average mercury content in hair of Huludao city inhabitants were 0.43 mg/kg. Effect of different age, occupation, gender, and living area of Huludao city residents was different to mercury in hair. The concentrations of Hg in different age groups decreased in the following order: young and middle aged > Youth >adolescent > the elderly (Hg). The gradual degradation of the digestive system of the elderly may make contribution to the reduction of heavy metals content in the hair. The average content of Hg in male resident's hair was roughly equal to that of female residents, but the content of male dispersion range was less than that of women. The average mercury content in blood of women was 1.75μg/L while these of children was 3.26 μg/L. Moreover, effect from Hg was much less than Pb and Cd for women and children.

4f: Science, policy, regulation: Global to local

MO-089

SCIENCE-BASED METRICS FOR GLOBAL MERCURY POLICY EVALUATION

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As the Minamata Convention enters into force and begins to be implemented, Article 22 requires evaluation of the effectiveness of the Convention beginning no later than six years after its entry into force and periodically thereafter at intervals to be decided. At the first Conference of Parties, the parties are tasked with establishing arrangements for providing comparable monitoring data on the presence and movement of mercury in the environment, as well as trends in biotic media and vulnerable populations. Based on analysis of scientific input into existing international environmental agreements, as well as literature on science-policy interactions, we review lessons learned in the area of effectiveness evaluation from scientific assessment processes at global scale. We recommend best practices for the design of assessments and institutions for scientific advice on mercury in the context of the Minamata Convention.

Building on this analysis, we explore how coordinated global-scale metrics might inform Convention decision-making on issues of long-range transport. As mercury poses both local and global pollution challenges, monitoring data reflects influences from a combination of sources, as well as environmental variability and the influence of global climate and other changes. From this perspective, we assess both science-based and policy-driven advantages and disadvantages of upstream metrics such as emissions, and downstream exposure-based measures (e.g. concentrations in biota), at various scales. While upstream metrics are characterized by less uncertainty and variability, downstream metrics are more directly relevant to stakeholder interests. Drawing upon lessons from global ozone and climate negotiations, we propose the development of a new global-scale metric to inform Minamata Convention implementation based on global mean mercury atmospheric concentration. Using an ensemble of simulations with the GEOS-Chem chemical transport model under differing climatic conditions and emission scenarios, we explore the statistical properties of such a metric, and its relationship with upstream and downstream alternatives. In comparison with existing data on atmospheric concentrations, we assess whether the current global monitoring network is sufficient to calculate a global mean concentration metric, and identify areas for improvement. We further assess the robustness of global-scale trends calculated with our metric relative to previous approaches.

MO-090

CANADA'S NORTHERN CONTAMINANTS PROGRAM – MONITORING CHANGES IN ARCTIC MERCURY IN RESPONSE TO GLOBAL EMISSIONS AND CLIMATE CHANGE

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For the past twenty-five years Canadas Northern Contaminants Program (NCP) has coordinated research and monitoring on transboundary pollutants in the Canadian North. These pollutants, including mercury, are present at relatively high concentrations in Arctic wildlife that are important food sources for Arctic Indigenous peoples, raising concern for their health and well-being. The primary objectives of the program have therefore been to a) inform and influence the development of policies and regulations that reduce sources of long-range pollutants; and b) provide information to health authorities for the development of public health advice and to Arctic Indigenous people so they can make informed dietary choices. Research and monitoring has addressed questions related to all aspects of contaminant cycling and impacts in northern ecosystems, from long-range sources and transport, to ecosystem and human health risks. Results are routinely published in peer reviewed journals, synthesized and published in comprehensive assessments, and communicated to national and international stakeholders.

Since 2004 the NCP has maintained a contaminant monitoring program that incorporates a variety of abiotic and biotic media that are sampled annually, or in the case of air, continuously, at prescribed locations. A primary objective for the program is to evaluate the effectiveness of international emissions regulations, such as those enshrined in the Minamata Convention. With few exceptions all monitoring is carried out in partnership with Indigenous communities, who in many cases take the lead on all aspects of field sampling. In the case of wildlife monitoring, data from annual sampling carried out since 2004 is augmented by data collected on a periodic basis from the 1990s, and in some cases the 1980s and 1970s. With the adoption of annual monitoring, the statistical power of these timeseries has recently improved to the point where relatively subtle trends are being measured with a reasonable degree of statistical significance.

The influence that global emissions have on mercury levels in wildlife must be assessed in the context of a changing environment. Climate related environmental change in the Arctic can affect all aspects of mercury cycling, including levels in wildlife. It is therefore important that monitoring be complemented by research that provides insights into how environmental processes are being affected by climate change. With the combined knowledge of both research and monitoring, it is possible to draw some conclusions on the relative impact that both changing emissions and a changing climate are having on wildlife exposure and trends.

MO-092

IMPLEMENTATION OF THE ENVIRONMENTAL QUALITY STANDARD (EQSBIOTA) UNDER THE EUROPEAN WATER FRAMEWORK DIRECTIVE IN FRENCH GUIANA FISH

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Mercury (Hg) is a toxic metal classified as a dangerous priority substance to be monitored in aquatic ecosystems by the European Water Framework Directive (WFD), due to its characteristics of bioaccumulation and biomagnification in food webs. An Environmental Quality Standard for biota (EQSbiota) has been defined for Hg in order to classify water bodies and was set at 0.02 mg Hg.kg-1 fresh weight. The application of such a standard requires defining one or more species of fish that is able to integrate the mercury contamination of the river in which they live. For this purpose, the WFD emphasizes the importance to choose species with a high trophic level (TL≥3) which corresponds to fish with the highest Hg concentrations (carnivorous and piscivorous species). Even considering an aquatic environment not exposed to direct inputs of Hg, fish with high trophic level are generally above the EQSbiota.

In French Guiana, we are faced with the difficulty of implementing this standard without downgrading all the aquatic ecosystems. Indeed, this region presents a great contamination of mercury due to the lithology of its soils and its history related to goldmining.

The aim of this study was to help designing appropriate monitoring program of Hg in fish for the implementation of EQS biota in this particular context. A database was created based on the mercury concentrations analyzed in fish muscle during 8 research programs carried out by the University of Bordeaux and the HYDRECO laboratory since 1990. Several difficulties have been encountered, particularly due to the difficulty to identify true reference sites and the high biodiversity of the ichtyofauna (416 known species). Two types of water bodies must be differentiated in French Guiana, due to their distinct hydrographic functioning: creeks (80% of the water system, very little studied) and rivers (20% of the water system). The database counts approximately 3000 fishes distributed over 50 creeks and 6000 fishes caught at about 200 stations located on the rivers of French Guiana; it includes also various information for each fish (Hg concentration in muscle, standard length, weight, family, species, trophic level, sample station location, anthropic or natural pressure for each station, etc.). The first results show that fish species in creeks are different from those present in rivers. After statistical and geographical data processing, 6 to 8 bioindicators species were proposed for creeks and 3 for rivers. The identification of reference sites, however, remains a very delicate task, due to the history associated with goldmining: just 7 potential reference sites for creeks and 4 for rivers. Results on Hg contamination of indicator fish species at reference and contaminated sites will be presented and discussed according to anthropogenic pressure. A first evaluation of reference concentrations is proposed.

MO-093

DEVELOPMENT, IMPLEMENTATION, AND CULTURAL IMPACT OF FISH CONSUMPTION ADVISORIES ON NATIVE AMERICAN TRIBES IN THE GREAT LAKES REGION

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Fishing and fish consumption are a vital component of the Anishinaabe bimaadiziwin, or tribal lifeway, of the Ojibwe tribes in the Lake Superior region. The presence of environmental contaminants in fish threatens both the continuation of this lifeway and the exercise of their treaty reserved rights to hunt, fish and gather off-reservation throughout the Ceded Territories in MN, WI, and MI. Here we describe the development of GLIFWCs mercury-based tribal fish consumption advisories which present culturally appropriate advice in the form of lake-specific, color-coded maps. We will also discuss our tribal outreach program for communicating safe fish consumption information, the efficacy of the consumption advisory maps, and the cultural impacts of fish consumption advisories on tribes.

MO-094

MERCURY CO-BENEFITS OF CLIMATE POLICY IN CHINA: ACHIEVING ENVIRONMENTAL AND SUSTAINABLE DEVELOPMENT GOALS

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National commitments on the Minamata Convention interact with other global environment and sustainability objectives, such as the Paris Agreement on climate change and the global Sustainable Development Goals. Understanding the interactions between mercury and other policy interventions can help decision-makers identify more effective policies that can address environmental and economic issues simultaneously. Here, we examine: 1) how Chinas national climate policy focused on decarbonization affects the countrys ability to meet its environmental goals related to mercury, and 2) how mercury reductions can contribute to overall national-level sustainability metrics. To address environmental goals, we assess how mercury co-benefits (positive side effects that are peripheral to a policys main goal) of a national climate policy in China could contribute to the countrys commitments under the Minamata Convention on Mercury. We examine climate policy scenarios in 2030 corresponding to various levels of carbon intensity reductions in addition to a business-as-usual scenario. Economic analysis from a computable general equilibrium model of Chinas economy (C-REM) provides information on changes in economic activity resulting from the climate policy scenarios. Using this economic data, we scale 2007 mercury emissions from the Emissions Database for Global Atmospheric Research (EDGAR) in a variety of sectors to 2030. We then use a global atmospheric transport model (GEOS-Chem) to project changes in mercury deposition at the regional scale in China for each policy scenario, and evaluate the resulting spatial distribution of mercury co-benefits. We compare our results to previous literature that considers end-of-pipe controls only for meeting Chinas commitments under the Minamata Convention on Mercury. To address sustainable development goals, we investigate the use of the Inclusive Wealth Index for evaluating the sustainability of climate policy in China on the basis of produced capital, natural capital, and human capital. We discuss the inclusion of mercury impacts in the natural capital and human capital components of the Inclusive Wealth Index by considering cropland, IQ impacts on labor and educational attainment, and other health effects (such as cardiovascular impacts) when data eventually become available.

MO-096

GOVERNING FORESTRY EFFECTS ON MERCURY - WHO OWNS THE PROBLEM?

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Fish Hg concentrations well above the Environmental quality standard set by the water framework directive (0.02 mg g-1 ww) are a major concern in large parts of Fennoscandia. Apart from anthropogenic Hg emissions to the atmosphere that deposits to forests far from the source of emissions there are catchment and lake characteristics that make Hg biomagnify effectively in aquatic food chains. Forestry operations can mobilize Hg from the soil, increasing Hg concentrations and loads in surface waters. Forestry activities might also cause waterlogged soils that make good habitats for Hg methylating microorganisms, increasing the formation of bioavailable methylmercury (MeHg). However, available forestry effect studies reveal considerable variation in treatment effects on MeHg at different sites, varying from no effect up to manifold concentration increases. Also, most available forestry effect studies focus on MeHg in low-order streams. When evaluating the effect of forestry on fish Hg concentrations it adds several layers of uncertainty associated with bioaccumulation. For management practices, it is hard to find solutions when the knowledge about different management strategies is complex.

Hg is not originally delivered by forestry itself, but from other human activities as well as natural sources. The forestry sector nevertheless has a responsibility to minimize the negative impact of harvest operations on the forests capacity to buffer and mitigate the pollution originating from other sectors. The issue of climate change has put additional demands on the forests to provide biomass as a substitute for fossil fuel. Thus, decision-makers are facing a wicked problem: How to reduce forestrys impact on Hg in aquatic ecosystems while securing other ecosystem services across the entire forestry cycle.

In order to explore forestrys responsibility and possible solutions to this problem in Sweden, a transdisciplinary approach has been used where actors from relevant governmental agencies, forest companies and forest associations have been involved. Through structured dialogue based in a risk governance approach, the character of the problem and possible ways to handled it were explored. The analysis shows that there are ways to handle the issue, but the complex character of the problem makes a need to include not only management practices for forestry but also the need to discuss regulatory goals and environmental objectives. The Hg-problem represents a class of difficult issues for forestry where the direct impact of forestry needs to be weighed against the contribution which that regulation can have on the overall issue.

1i: Comparable measurement results for mercury analysis and speciation

TO-001

A NOVEL GRAVIMETRIC PRIMARY MERCURY VAPOUR STANDARD

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Within the "Traceability for mercury measurements" project (MeTra; European Metrology Research Programme) a mercury vapour generator is being developed to establish traceability of mercury vapour measurement results, based upon a gravimetric approach, for ambient air levels as well as higher concentrations.

Current measurement capabilities are maintained at levels of 0,25 – 350 µg Hg/m3, whereas the aim of the novel gravimetric primary standard is to realize metrological traceability for the range 5 ng Hg/m3 - 60 µg Hg/m3, with a target measurement uncertainty of 1 %. This to cover key requirements for ambient air monitoring (1 - 2 ng Hg/m3), health-based exposure standards (50 ng Hg/m3), concentrations relevant to stationary source emissions (upwards of 1 µg Hg/m3) and the minimum alveolar concentration value (20 µg Hg/m3).

The development and characterization of the primary vapour generator will be presented. Furthermore the results will be presented of two comparisons held to demonstrate the robustness and comparability of the novel primary standard. One comparison was performed against the Dumarey vapour pressure equation, while another comparison was performed against current calibration facilities present at national metrology institutes.

The newly developed mercury vapour generator will contribute to comparable measurement results of mercury vapour at ambient and background air levels, and also to higher safety standards and cost reductions in e.g. the LNG field, where aluminium main cryogenic heat exchangers are used which are particular prone to corrosion caused by mercury.

TO-002

DEVELOPMENT AND TESTING OF A GEM STANDARD ADDITION SYSTEM TO A SPECIATED MERCURY ANALYZER

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A standard addition system was developed that utilizes the Gaseous Elemental Mercury (GEM) output from a Tekran(r) 2537X permeation source and ports it to the entry glassware of a speciated mercury system. Valve timing and control is performed using National Instruments LabVIEW(r) software. At our Atmospheric Mercury Network (AMNet) site in Beltsville, MD standard addition spikes are made into the inlet sample flow at points upstream and downstream of the inlet impactor frit during both GEM sampling and desorption periods. This allows ambient and zero-air matrix effects to be investigated, and provides a measure of any losses of GEM in the complete sampling train. From these spikes an effective response factor is derived and compared to that obtained using calibrations through the internal flow path of the 2537X analyzer. Applying interpolated effective response factors to each five-minute integrated ambient GEM sample reduces the within-hour standard deviation by correcting matrix-effect trap bias, and also results in an increase in hourly-averaged GEM measurements. Changes in standard addition instrument response are correlated with meteorology and trace gas measurements.

TO-003

ADVANCE ON MERCURY ISOTOPES METROLOGY

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The assessement of Mercury impact on ecosystems and human health is of major concern and European Directives are waiting for a real traceability procedure on its measurement as well as the reduction of the associated uncertainties. Reliability and comparability of mercury measurements are essential to assess concentrations and trends of this highly toxic element. The European Project JRP ENV51 MeTra Traceability for Mercury Measurements aims to meet these needs in the different environmental compartments.

Recently, the exploration of mercury isotopes allows the discrimination of Hg sources for a better understanding of its biogeochemical cycle in the environment. Many factors control Hg isotopes fractionation in the environment such as biological or photoreduction processes leading to a specific isotopic fingerprint in the final product. To ensure the quality and validate these measurements, it is necessary to understand and control all the fractionation processes which can occur during each steps of the analytical chain (sampling, storage, sample prep) but also during the sample introduction (CVG/GC) and the analysis on the MC-ICP-MS.

To evaluate of all these potential sources of fractionation, we have controled in detail the whole analytical chain for Hg factionation in environmental samples. At first, we have studied the storage condition of the sample by measuring several NIST 3133 solution over a long time period. The accuracy and precision of different sample preparation (digestion/derivatization) and different sample introduction (several CVG, GC) were assessed by comparing HotBlock, Microwave and High Pressure Asher digestion as well as derivatization step which is critical for compound specific isotopic analysis which can lead to inaccuracy on total mercury budgets. Further, depending on digestion methods used or reactives introduced, matrix effects can occur during the Hg isotopes analysis. We have therefore investigated several compounds added to standard solution such as oxydant (H_2O_2, BrCl) or organic matter in order to understand the potential fractionation induced during measurements. Finally, mass discrimination in the MC-ICP-MS can play a major role on isotopic fractionation and mass bias correction by Tl internal standard, which can be also mass discriminated, can lead to an underestimation of the analytical uncertainty. This implies that different mass bias correction methods were explored by comparing sample-standard bracketing and internal standard correction method. We will present and discuss all the potential biais that may be introduced during Hg isotopic fractionation measurements in environmental samples all along the analytical chain.

TO-004

YES, YOU CAN MEASURE MERCURY IN THE FIELD WITH ACCURACY, PRECISION, AND SENSITIVITY

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Field techniques for measuring Hg in contaminated soils have always been an appealing prospect. In situ field measurements have the potential to provide significant savings in sampling, shipping, and laboratory costs. More importantly, the real-time reporting of field instruments can greatly increase the efficiency of monitoring efforts by quickly locating hotspots, making real-time decisions to develop more targeted sampling strategies, and efficiently delineating contaminated areas in the field.

Handheld X-ray fluorescence spectrometers (XRF) provide a rugged and portable style that is ideal for in situ monitoring. Many researchers have successfully used XRF for field screening of Pb, As, and other metals at contaminated sites, however, previous attempts at using handheld XRF for Hg analysis have been disappointing. Devices have typically provided insufficient sensitivity or poor accuracy and precision.

In this study, we demonstrated that handheld XRF can be successfully used in the field to measure Hg in soils with accuracy, precision, and sensitivity. Rather than using manufacturer configurations and calibrations, this study developed a Hg-specific calibration set and used Hg-specific configurations to optimize sensitivity and increase the accuracy of Hg detection. This study measured 239 bank soil samples in the field at the South River remediation site in Waynesboro, Virginia. After field analysis using the handheld XRF, samples were shipped to a laboratory for confirmatory Hg analysis using EPA Method 7471A.

The handheld XRF was able to achieve a method detection limit of 7.4 mg/kg Hg with a 60-second analysis time, sufficient for comparison to most risk-based soil screening levels. Accuracy of the XRF method was determined by analysis of spiked Hg samples and by comparison of field results to laboratory Method 7471A results for the 239 collected samples. Percent recovery for spiked samples averaged 102%, and the regression of spiked Hg levels to XRF reported values achieved an R2 value of 0.999. XRF and Method 7471A results were highly correlated with an R2 value of 0.934. Precision of the method was determined by the analysis of field triplicates. The median CV (coefficient of variation) for XRF field triplicates was 18%, compared to a median CV of 19% for field duplicates measured using Method 7471A. These findings demonstrate that the XRF method, if calibrated and optimized properly for Hg, can be used to quickly and reliably analyze the Hg content of soils in the field with sufficient accuracy, precision, and sensitivity.

TO-005

COMPARABLE MEASUREMENT RESULTS FOR GLOBAL MERCURY MONITORING IN THE MARINE ENVIRONMENT

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The launch of the United Nations Environment Programme Global Legally Binding Treaty on Mercury, will lead to the establishment/strengthening of Mercury monitoring efforts of the countries in different environmental compartments, in order to assess environmental mercury contamination, as well as to control the efficiency of the control measures undertaken. Therefore, Mercury monitoring will become an integral part of all marine monitoring programmes implemented at national or/and regional level around the world. Because of the expected proliferation of the generated Mercury monitoring data, and taking into consideration the difficulties related to the accurate analysis of Mercury and its species in marine samples, the use of recommended analytical methods by the laboratories involved in this effort, as well as the strengthening of the quality assurance of their data, is a necessity for the effective use of the generated data for environmental assessments and decision making. Therefore, many developing countries will need assistance to build their capacity for accurate and representative mercury analysis in the marine environment.

To assist countries in the strengthening of their Mercury data quality assurance, the Marine Environmental Studies Laboratory of IAEA is developing fit-for-purpose recommended analytical methods for Mercury and Methyl Mercury in marine sediment and biota, organises Inter-Laboratory Comparison (ILC) exercises and produces relevant Certified Reference Materials to be used by laboratories involved in mercury monitoring in the marine environment. Recently MESL has produced one new CRM for Mercury and Methyl Mercury in marine sediment and two CRMs in biota samples (clam and scallop). The Recommended Methods for Mercury and Methyl Mercury, as well as the relevant CRMs in marine sediment and biota, will be outlined in the presentation.

TO-007

LOW UNCERTAINTY MEASUREMENTS TO CHARACTERIZE THE ACCURACY OF COMMERCIAL, NIST-TRACEABLE HG0 AND HGCL2 REFERENCE GAS STANDARDS.

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Gaseous elemental mercury (Hg0) and oxidized mercury (HgCl2) reference standards are integral to the use of mercury continuous emissions monitoring systems (Hg CEMS) for regulatory compliance emissions monitoring. EPA and NIST have collaborated to establish the necessary procedures for establishing the required NIST traceability of commercially-provided Hg0 and HgCl2 reference generators. However, a quantitative disparity of approximately 7-10% has been observed between commercial Hg0 and HgCl2 reference gases which currently limits the use of (HgCl2) reference gas standards. The source of this disparity is the focus of considerable debate. Moreover, the actual disparity has not been accurately quantified. This presentation will highlight the approach and results of a joint NIST/EPA study to accurately quantify the true concentrations of Hg0 and HgCl2 reference gases produced from high quality, NIST-traceable, commercial Hg0 and HgCl2 generators. The results of this study will not only quantify the disparity, but will help provide an understanding of the source of this disparity, if confirmed.

TO-008

EVALUATION OF MERCURY POREWATER CONCENTRATION MEASUREMENT APPROACHES AND THEIR SIGNIFICANCE AND BIOLOGICAL RELEVANCE

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Mercury porewater measurements are an important indicator of mobility and availability of mercury in natural systems. Mercury associated with the solid phase is typically not as available for uptake or methylation as mercury present in porewater in either dissolved or suspended phase. Techniques for evaluating porewater mercury concentrations include direct withdrawal of porewater, collection of minimally disturbed sediment cores for processing via porewater displacement or centrifugation, as well as passive sampling techniques including dialysis membrane sampling devices (peepers), and flux based diffusive gradient in thin film samplers (DGTs). Direct withdrawal is difficult in fine-grained low permeability media and often difficult to ensure that only porewater is collected. Porewater expression from cores can be effective but care must be taken to avoid disturbance of the core. Centrifugation is often used but resuspend colloidal and suspended particles that can then scavenge dissolved mercury during filtration. All of these methods suffer from sensitivity to the filtration approach (e.g. sensitivity to filtration size).

As compared to previous techniques, passive samplers have advantage of greatly reducing the disturbance of the physical and chemical conditions present at the site. Dialysis membrane passive samplers typically require collection of relatively large volumes potentially limiting vertical resolution and lengthening sampling time. Diffusive Gradient in Thin-Film (DGT) samplers require relatively short exposure times and exhibit low detection limits by concentrating mercury or methyl mercury on a sorbing resin. A concern with both methods is the question of the relationship of mercury speciation and the measurement obtained by the sampler. In our research, we have investigated the mercury species and complexes most likely to be measured by DGTs and used a combination of microbial and macrobenthic assays to show that these species and complexes are the most likely to be biologically relevant.

This paper compares these various approaches to the measurement of mercury in porewater. The relative strengths and weaknesses of each approach and their biological relevance will be identified. The specific advantages of DGTs for the assessment of mobile and bioavailable mercury will be emphasized and the rationale behind expanding use of DGTs identified.

2b-1: Sources and cycling of mercury in freshwater ecosystems

TO-009

EVALUATING THE INFLUENCE OF SEASONAL STRATIFICATION ON MERCURY METHYLATION RATES IN THE WATER COLUMN AND SEDIMENT OF A WESTERN US RESERVOIR

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Mercury (Hg) methylation often occurs at the active redox boundary between oxic and anoxic conditions in sediment and the water column of lakes. Previous studies have suggested that sediment methylation rates are highest when the overlying water is oxygenated and that during periods of stratification the predominant zone of methylation activity switches from the sediment to the water column. However, studies that simultaneously measured methylmercury (MeHg) production in the water column and sediment remain limited. Understanding the relative importance of sediment versus water column methylation and how this changes in response to seasonal stratification has important implications for management strategies aimed at reducing MeHg production, such as hypolimnion oxygenation. Our study measured Hg methylation and demethylation rates using inorganic Hg and MeHg stable isotope tracers in sediments and water of the littoral zones and deeper central waters of a reservoir in Californias central coastal range. Measurements were conducted during well-mixed/oxygenated conditions (winter) as well as at the beginning (spring) and end of thermal stratification (late-summer). We also evaluated how variations in the isotope spike solution (using DI water, ambient water, carbon enriched water) affected the methylation rates. These results found the lowest methylation rates were associated with the DI isotope spike solution, suggesting that microbial community prefers Hg bound to a carbon source. The results from the field sampling showed that the ambient MeHg concentrations were very high in the hypolimnetic waters (up to 7.5 ng/L representing up to 79% MeHg/THg) during periods of stratification. During the late summer, the sediment in the littoral zones underlying oxic water had significantly higher methylation rates (2.4 %/day) compared to the sediments underlying anoxic water in the hypolimnion (1.3 %/day). Sediment demethylation rates were much higher in sites under the anoxic hypolimnetic waters (9.8%/day), compared to the littoral sediments with overlying oxic water (2.2 %/d). These results highlight the importance of net MeHg production in the littoral zones. Following turnover, methylation rates in this deep section of the reservoir did not increase when the overlying water became oxygenated. Under anoxic conditions, water-column methylation rates were of similar magnitude to the sediment (3.0 %/day) and were insignificant in oxygenated water. Taken together, these results suggest that methylation in the water column provides a significant source of MeHg to the reservoir, and that following turnover when water-column methylation ceases, there is not a concomitant shift towards higher production in the sediments.

TO-010

RESPONSES OF MONOMETHYLMERCURY ACCUMULATION IN FISH TO THE TROPHIC STATES OF ARTIFICIAL TEMPERATE RESERVOIRS

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The aim of this study is to understand the correlation between MMHg concentrations in fish and trophic states of different reservoirs. For this purpose, we investigated MMHg concentrations in 466 samples of four common fish species (barbel steed, largemouth bass, leopard mandarin, and bluegill) and trophic states of 14 artificial reservoirs in South Korea. The trophic state index (TSI) of each reservoir was determined using empirical equations based on the monthly chlorophyll-a, total phosphorus, and Secchi depth collected over a three-year period. The length-normalized MMHg concentrations in fish (MMHgadj) showed a negative correlation with the TSI based on total phosphorus (r2 =0.75), which might be a result of particle dilution of MMHg in surface waters. A log-normal correlation was found between the fish MMHgadj and the TSI based on chlorophyll-a (r2 =0.76), attributable to low chlorophyll-a concentrations, despite of the high particle densities, in the oligotrophic reservoirs. This study is the first to reveal MMHg accumulation in fish via the relationship with TSI of the lakes, suggesting that the measurement of TSI based on chlorophyll-a and total phosphorus is an effective way to predict MMHg bioaccumulation across diverse reservoirs.

TO-011

MERCURY METHYLATION IN THE WATER LEVEL FLUCTUATION ZONE OF CHINA'S LARGEST HYDROELECTRIC RESERVOIR: THE ROLE OF INORGANIC SULFUR REDOX CYCLING

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The Three Gorges reservoir (TGR) is the largest hydroelectric reservoir in

China, with a total water surface area of 1080 km2 and a storage capacity of 39.3 billion m3. Hydroelectric regulation results in a water-level fluctuation zone (WLFZ) with a total area of 306.3 km2 that undergoes annual flooding and drying alternating cycles. The alternating redox conditions in this WLFZ make it a very interesting area for the cycling of mercury (Hg) and sulfur (S), although the effect of the S redox cycle on Hg methylation is not clear. Sulfide may reduce the availability of Hg through immobilizing mercuric ions as sparingly soluble HgS(s). On the other hand, the dissolved mercury-sulfide (Hg-S) complexes formed in a sulfidic environment may facilitate Hg methylation. Here we present the results from a year-long monitoring of the WLFZ, as well as a flooding and drying simulation experiment with elemental sulfur (S0) addition. Field studies showed that the concentrations of both methylmercury (MeHg) and reduced S in the WLFZ were significantly higher than that in non-flooded soils. Significant positive correlations were found between MeHg and S0 ($p < 0.01$), acid volatile sulfide (AVS) ($p < 0.01$), pH ($p < 0.05$) and soil organic matter ($p < 0.01$) in soil/sediment of the WLFZ. In the flooding and drying simulation experiment, S0, which is an intermediate product of sulfate reduction and sulfide re-oxidation, showed a higher correlation ($r = 0.74$, $p < 0.05$) with MeHg when compared to field samples. In the S0 added anaerobic sediment, the correlation coefficient of S0 and MeHg was even higher ($r = 0.86$, $p < 0.01$) when the content of dissolved organic matter was held constant. These relationships indicate that S0 in the redox alternating WLFZ environment could promote MeHg production especially under reducing conditions. This could be due to the formation of polysulfides from reactions of S0 and sulfide, which are known to increase the concentrations of dissolved Hg from the solid HgS pool in the soil. The periodic regulation of the water level in the TGR and the resulting redox cycling of inorganic sulfur in the WLFZ may thus enhance the production of MeHg in both aquatic and terrestrial ecosystems.

TO-012

A REVIEW OF MERCURY RESEARCH IN FRESHWATER ECOSYSTEMS ACROSS THE GLOBAL BOREAL ZONE

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Mercury (Hg), a neurotoxin with a global atmospheric distribution, has been shown to readily deposit onto northern landscapes where it can enter freshwater systems and bioaccumulate in sport and subsistence fish. However, the biogeochemical cycle of Hg, including bioaccumulation, is complex and influenced by many physicochemical and ecological factors. While several recent reviews have been published on the factors that affect aquatic Hg cycling in the Arctic, reviews on Hg research in the global boreal zone are lacking. The main goal of this review was to assess which physicochemical parameters (e.g., DOC, pH, Lake size) significantly affect Hg concentrations in boreal waters, sediments, peatlands, invertebrates, and/or fish in 5 key boreal regions: North America, Fennoscandia, Russia, China, and other countries (e.g., Estonia). A total of 673 correlative relationships were found between various physicochemical parameters and abiotic and biotic Hg concentrations in freshwater systems across these regions. No major spatial differences were found in the direction of the relationships reported between Hg concentrations and a given physicochemical parameter. Consistent positive relationships were frequently reported between Hg concentrations in water, sediments, and biota and aqueous organic matter (OM) content as well as certain watershed characteristics (e.g., % forested or wetland area) of freshwater boreal systems, suggesting that terrestrial Hg is transported into freshwater systems by OM complexes. Conversely, base cations were negatively correlated with Hg concentrations in boreal sediments, invertebrates, and fish, potentially due to an inhibition of Hg methylation and increased competition for binding sites on OM complexes. In addition to assessing these correlative relationships, we compiled data on Hg in fish muscle from 92 studies across the boreal region and found that perch (Perca flavescens in N. America and Perca fluviatilis in Fennoscandia/Russia) had significantly lower length-standardized (at 14 cm) total Hg concentrations in Fennoscandian lakes (0.176±1.097 ppm, wet weight) compared to North American (0.356±1.108 ppm, wet weight) and Russian (0.471±1.320 ppm, wet weight) lakes. Results from this review will provide valuable insight into which physical and chemical factors control Hg cycling across the boreal zone. We also discuss the implications of these results in the context of anticipated changes to boreal landscapes due to various types of industrial development (e.g., forestry, mining, and hydropower), which are expanding across the boreal.

TO-013

VARIABILITY IN AND TIMES TO RECOVERY FROM MERCURY POLLUTION FOR MICHIGAN LAKES

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Anthropogenic emissions combined with long-range transport and atmospheric deposition have contributed to a state-wide fish consumption advisory for mercury (Hg) in Michigan. Lake sediment cores in Michigans Upper Peninsula (UP) indicate that Hg accumulation increased approximately 3-fold above background rates. There are conflicting predictions as to the future trajectory for Hg deposition and for the recovery of lakes from that deposition. Concentrations of Hg in Michigan rivers and lakes increased over the past two decades during which time atmospheric deposition declined. Furthermore, the geographic pattern of concentrations in lakes and fish does not match the pattern of atmospheric deposition. Accurate prediction of the future recovery of lakes requires an understanding of the magnitude and timing of mercury runoff from terrestrial catchments as well as understanding of the rate of cycling of mercury within the lake and food web.

This study applied both a statistical and a mechanistic modeling approach to meet the two objectives: 1) to determine the causes of variability for mercury in lakes of the UP, and 2) to predict the time required for fish from UP lakes to be safe for unlimited consumption. We examined the spatial distribution of mercury in lakes, fish, rivers and atmospheric deposition across the Upper Peninsula (UP) of Michigan. Multiple data bases were combined to estimate the magnitude of mercury runoff from catchments, the best predictor variables for mercury concentrations in lakes, and the factors best explaining methyl mercury (MeHg) concentrations in fish. The statistical analyses enabled us to create categories of lakes having similar fish mercury, and to apply a Hg cycling model to predict the timeline for recovery under different scenarios for Hg deposition.

This study indicates that the magnitude of mercury runoff from catchments has been much less (5-15% of atmospheric deposition) than estimated by previous studies (~25%). Large variations in dissolved Hg concentrations as well as mercury content in fish among lakes in Michigans Upper Peninsula (UP) suggest that runoff may be highly variable among catchments, but the major rivers in the UP show remarkable uniformity in runoff. While DOC is an important explanatory variable for dissolved mercury in lakes, the DOC is not well predicted by wetland areas. For mercury in fish, lake pH is the most significant predictor variable, but lake size is also important. The time to recovery depends primarily on the regulations imposed on emissions and on the timescale for run-off from catchments.

TO-014

RECYCLING OF MARINE MERCURY IN MOUNTAIN LAKES

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Over the last decade, a rapidly evolving interest in mercury's (Hg) isotopic composition have shed light on the pathways and chemical forms Hg undertakes, along with identification of contributing sources to the complex global Hg-cycle, yet many questions remain regarding source and trophic transfer of Hg in natural systems. Marine and fresh-water food webs, and the Hg isotopic composition within them, are often investigated separately and treated as two distinctly different ecosystems with little overlap between them. An exception to this is fish farms, where fresh-water fish is bred and raised on a man-made and atypical high energy diet, which main protein source is based on fishery products of marine origin. Yet, the effect on natural ecosystems of non-native fish, raised on a marine protein based diet, in a geochemical perspective in general, and in the scope biomagnification of Hg and Hg-isotopes specifically, is still unknown. Using a combined geochemistry (THg) and stable isotope (N, C, Sr and Hg) approach, we here show that the introduction of farmed brown trout (Salmo Trutta Fario) to a high-altitude catchment leads to a small, yet relevant, input of directly bioavailable MeHg and to a recycling of marine Hg, which potentially clouds the isotopic signature of Hg in the natural system. We found that farmed trout show Hg-isotopic signatures directly comparable to that of marine and off-coastal biota whereas wild trout indicated Hg-isotopic signatures related to atmospherically derived Hg and photochemical processes. The stocked, farm-rearing fish, showed Hg-isotopic signatures more similar to the marine and coastal biota, but as the trout evolved and shifted its diet to a higher trophic level, gaining an overall higher THg-concentration, the marine farmed rearing signature was diluted by the atmospherically derived Hg, rendering in lower MDF (mass dependent fractionation, δ202Hg) and higher MIF (mass independent fractionation, Δ199Hg). In contrast to the current status quo on global Hg-cycle, i.e. that bioaccumulated MeHg biomagnifies up the food chain we here claim that in watersheds subject to stocking of farmed fish, Hg does not only bioaccumulate and biomagnify, but also re-biomagnifies, thus leading to inherent difficulties when deciphering the ecological pathway of Hg transfer on global scales, but also locally i.e. through the food web within an aquatic system.

TO-015

MERCURY TEMPORAL TRENDS IN TOP PREDATOR FISH OF THE LAURENTIAN GREAT LAKES FROM 2004 TO 2015: ARE CONCENTRATIONS STILL DECREASING?

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Mercury (Hg) concentration trends in top predator fish (lake trout and walleye) of the Great Lakes (GL) from 2004 to 2015 were determined by Kendall−Theil robust regression with a cluster-based age normalization method to control for the effect of changes in lake trophic status. When data from the GLs (except Lake Erie) are combined, a significant decreasing trend in the lake trout Hg concentrations was found between 2004 and 2015 with an annual decrease of 4.1% per year, consistent with the decline in regional atmospheric Hg emissions and water Hg concentrations. However, a breakpoint was detected with a significant decreasing slope (−8.1% per year) before the breakpoint (2010), and no trend after the breakpoint. When the lakes are examined individually, Lakes Superior and Huron, which are dominated by atmospheric Hg inputs and are more likely than the lower lakes to respond to declining emissions from areas surrounding the GL, have significant decreasing trends with rates between 5.2 and 7.8% per year from 2004 to 2015. These declining trends appear to be driven by decreasing regional

atmospheric Hg emissions although they may be partly counterbalanced by other factors, including increasing local emissions, food web changes, eutrophication, and responses to global climate change. Lakes Michigan, Erie and Ontario may have been more impacted by these other factors and their trends changed from decreasing to non-decreasing or increasing in recent years.

TO-016

MERCURY PHOTO-REDUCTION AND TOTAL PHOTOREDUCIBLE MERCURY DYNAMICS IN THE LAKES OF KEJIMKUJIK NATIONAL PARK, NOVA SCOTIA

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Photo-reduction and photo-oxidation are fundamental mechanisms controlling mercury volatilization and accumulation in freshwaters. In all surface waters dissolved gaseous mercury (DGM) is produced as a net result of the reduction of reducible mercury, which is believed to be primarily divalent mercury (Hg(II)) bound to specific carbon-based ligands, and the oxidation of elemental mercury (Hg(0)). These two processes control the amount of DGM available for evasion across the water-air interface; however, determination of the fundamental rate constants and mechanisms of these reactions in freshwaters are still areas that require more research. In particular, the total amount of photoreducible mercury is emerging as a key variable that requires more exploration.

Here, we review the progress our group has made in this field over the past 10 years; we present rate constants as well as temporal dynamics in total reducible mercury derived from two recent projects that examined water samples from a series of freshwater lakes in Kejimkujik National Park, Nova Scotia, Canada. We examined the hypothesis that gross photoreduction and photooxidation rates would be significantly different in lake water. Another hypotheses was that the amount of mercury available for reaction with solar radiation (i.e. reduction of Hg(II) to gaseous Hg(0)) in surface waters would significantly change over a summer. A Luzchem photo-reactor was used to irradiate 200 mL water samples in quartz beakers continuously exposed to ultraviolet radiation for 24 h with concurrent Hg(0) analysis to derive pseudo-first order gross reduction rate constants and batch experiments were used to derive net reduction rates (and gross photooxidation by difference).

Results showed that the net photo-oxidation rates for freshwaters were low, with mercury reduction and oxidation reactions very close to being in balance. We also found that the amount of total reducible Hg(II) changed significantly in three of the lakes over several sampling months. Dissolved organic carbon concentration was a key factor positively correlated with these results. This research provides the first quantitative measurements of gross photooxidation and photoreduction rates as well as total photo-reducible mercury over a season in surface freshwater lakes.

2f-3: Mercury methylation: microbial and geochemical constraints

TO-017

MERCURY BIOMETHYLATION IN BIOMINING-AFFECTED SULFIDE-RICH AND NATURAL SEDIMENTS RETRIEVED FROM BOREAL DYSTROPHIC LAKES

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Freshwaters throughout the Globe are contaminated by mercury (Hg) due to anthropogenic activities. Considerable part of the global atmospheric Hg deposition takes place in boreal regions. Biomining that exploits bacterial leaching on-site is suggested as a clean technology to recover metals from low-grain ores. However, biomining effluents have been shown to cause salting and multi-metal contamination of the effluent-receiving waterways. Risk assessors are challenged by the multitude of adverse effects biomining effluents are suggested to have towards freshwater ecosystems. Of those the potential enhancement of Hg biomethylation to methylmercury (MeHg) is surely not the least in importance. Mercury biomethylation in surficial sediments can become enhanced due to sulfate-containing effluents that enhance hypoxic and anoxic conditions in the lake bottoms that again favor activity of sulfate reducing bacteria besides of the sulfate addition itself. These bacteria can methylate Hg to MeHg that biomagnifies in the food web. We sampled surficial sediments from biomining-affected Lake Kalliojärvi and Lake Jormasjärvi, the sedimentary basin of the latter being mixed on the spot, and from one non-mining-affected Lake Ukonjärvi. The sediments showed Hg accumulation at 106.9 (L. Kalliojärvi), 293.1 (L. Jormasjärvi) and 372.1 (L. Ukonjärvi) ng Total Hg g-1 dw with MeHg proportions being 3.8, 0.6 and 1.2 % of Total Hg (THg), respectively. We incubated the sediments at laboratory set-ups for 14 days with their natural bacteria present with two treatments: 1) normoxia and 2) hypoxia in the sediment overlaying water, measured the THg-MeHg proportions in the sediments thereafter and compared them to various water and sediment characteristics. The results indicated our hypotheses that 1) hypoxia enhances Hg biomethylation compared to normoxia in the non-mining-affected sediment, and that 2) the mining-affected anomaly-sediments likely show deviation from this phenomenon, were true. In the heavily contaminated L. Kalliojärvi sediment the highest proportions of MeHg were measured at 14-d with some but not as evident hypoxia effect as in the non-mining-affected L. Ukonjärvi sediment. In the moderately mining-affected L. Jormasjärvi sediment there was no difference between the treatments in Hg biomethylation. Methylmercury in sediment correlated negatively with redox potential in the overlaying water, sediment dry matter content and iron concentration (Pearson's r-values: -0.31 - -0.55), and positively with water sulfate and iron concentrations (0.59-0.69). Mercury biomethylation can be enhanced in mining-affected sediments. Yet the conditions favorable for Hg methylation are complex, and enhancement of Hg biomethylation will probably not always be the prevailing case in mining-affected freshwaters.

TO-018

EFFECTS OF MERCURY ADDITION ON MICROBIAL COMMUNITY COMPOSITION AND MERCURY METHYLATION INSIDE PERMEABLE REACTIVE BARRIERS

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Permeable reactive barriers (PRBs) remove nitrogen from groundwater by enhancing denitrification. The PRBs consist of woodchips that provide a virtually unlimited carbon source for heterotrophic denitrifiers. This carbon also supports other anaerobic bacteria, some of which, including sulfate-reducing bacteria (SRB), have the ability to methylate inorganic mercury that occurs in groundwater in industrialized areas. We examined microbial community composition and geochemistry in flow-through PRB mesocosms, half of which were spiked with sulfate throughout the experiment to simulate a salt water environment. Halfway through the experiment, we began spiking all replicates daily with mercuric chloride. We hypothesized that mercury addition would alter community composition to favor higher abundances of known methylating taxa, and that the sulfate mesocosms would produce more methylmercury than the non-sulfate mesocosms due mainly to an increase in abundance of SRB. We found that taxa of SRB, including desulfobacterales, were more abundant after spiking with mercury, while taxa inhibited by Hg, like arcobacter, decreased. We also found a period of adjustment after the start of Hg spiking, where nitrate removal became incomplete and methylmercury production was low, but after two days, nitrate removal became complete again and methylmercury production rose. Overall, however, there was no net increase in methylmercury production over the course of the experiment, and no significant difference in production between sulfate and non-sulfate treatments. This could be due to inhibition of methylation from high sulfide concentrations, or demethylation by microbes possessing the mer operon, which were also more abundant after spiking with mercuric chloride.

TO-019

MICROBIAL DEMETHYLATION IN THE ENVIRONMENT: ROLES OF IRON-REDUCING BACTERIA AND METHANOTROPHS

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Microbial methylation and demethylation are two competing processes controlling the net production and bioaccumulation of neurotoxic methylmercury (MeHg) in natural aquatic environments. Although mercury (Hg) methylation by anaerobic microorganisms and demethylation by aerobic Hg-resistant bacteria have both been extensively studied, little attention has been given to microbial degradation of MeHg, particularly by anaerobic iron reducers and aerobic methanotrophs, despite their ubiquitous presence in the environment. We report that the iron-reducing bacterium Geobacter bemidjiensis Bem can both methylate inorganic Hg and degrade MeHg concurrently under anoxic conditions. A reductive demethylation pathway is likely utilized by G. bemidjiensis to degrade MeHg, with elemental Hg(0) as the major reaction product, possibly due to the presence of homologs encoding both organo-mercurial lyase (MerB) and mercuric reductase (MerA) in this organism. Additionally, G. bemidjiensis Bem cells can mediate multiple reactions including Hg sorption, reduction and oxidation, resulting in both time and concentration dependent Hg species transformations. For the first time, we also demonstrate that some methanotrophs (e.g., Methylosinus trichosporium OB3b) can take up and degrade MeHg rapidly despite they do not possess merB or merA in their genome. Demethylation by M. trichosporium OB3b increased with increasing MeHg concentrations (up to ~75 nM), but a high MeHg concentration (125 nM) decreased demethylation due to MeHg toxicity. Unlike many known Hg-methylators, all methanotrophs are found to take up substantial amounts of MeHg, likely as a one-carbon (C1) growth substrate and energy source. These findings indicate a cycle of methylation and demethylation among anaerobic and aerobic bacteria, and suggest that both anaerobic iron reducers and aerobic methanotrophs may play an important role in the net balance of MeHg production in the environment.

TO-020

SUPPRESSION OF METHYLMERCURY PRODUCTION AND TRANSPORT IN SEDIMENT USING IRON (FERRIC) OXIDE

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Tests on natural sediments were performed to measure the effect of ferric oxide on mercury methylation and mobility, by shifting the

microbial community and increasing the sorption capacity of the sediment. Iron oxide treatment was tested on replicate chambers having either oxic or anoxic overlying water, and untreated controls were tested on replicate chambers simultaneously. A single treatment of slurried ferric oxide was injected into the top 2 cm of sediment at a density of 0.50 moles/m2 (28 grams as Fe+3), and the chambers allowed to run for 6 months. Overlying water and sediment were periodically sampled to track the evolution of the chambers.

After 6 months, the mass of methylmercury in the top 2 cm of iron-treated sediment decreased by an average of 40% compared to controls, while the mass increased in the 3-5 cm interval by an average of 20%. The center of mercury methylation deepened from 1 to 4 cm, which decreased the availability of sulfate to SRB and increased the upward diffusion distance of methylmercury to the overlying water by a factor of four. The concentration of methylmercury in the top 3 cm of porewater of iron-treated sediment was below detection (<20 pg/L), while the untreated anoxic control averaged 350 pg/L. The concentration of methylmercury in overlying water of both oxic and anoxic iron-treated sediments was below 20 pg/L, while the anoxic control was 270 pg/L. Upward transport and release of methylmercury to the overlying water was limited by sorption onto the iron oxide, which increased the bulk partition coefficient from 3,000 in the anoxic control to 30,000 in the anoxic iron-treated sediment. The results show that iron oxide treatment can be effective in suppressing mercury methylation and release even in systems with anoxic water columns.

TO-021

IDENTIFYING DRIVERS OF MERCURY METHYLATION AROUND GIANT MINE, YELLOWKNIFE

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Mercury (Hg) is a global pollutant and potent neurotoxin that bioaccumulates in aquatic and terrestrial foodwebs as monomethylmercury (MMHg). Microbial activity is the main driver of MMHg production, with sulfate reducing bacteria being important contributors. As such, predicting MMHgs fate in the environment is important for addressing ecosystem and human health concerns. The roasting of arsenopyrite at Giant Mine in Yellowknife, Canada, has created strong environmental gradients of sulfate in lakes in the surrounding area with distance from the mine. Whereas total Hg levels remain constant with increasing distance from the mine, the ratio of MMHg relative to total Hg increases with proximity to the stack. We hypothesized that the sulfate gradient is responsible for the pattern of MMHg concentrations around Giant Mine. As such, a factorial sampling design was developed to resolve whether sulfate or other environmental variables were affecting the production of MMHg in the lakes surrounding Giant Mine. To test our hypothesis, we sampled water and sediments from various lakes around Giant Mine. Using stable isotope analysis we determined simultaneous methylation and demethylation potentials, and defined the environmental variables affecting these rates of mercury cycling. Furthermore, we characterized the sediment microbial community structure using high throughput sequencing of 16S rRNA genes and physical chemical variables of the lakes sampled.

TO-022

MERCURY METHYLATORS AND METHYLATION RATES IN SULFATE-IMPACTED FRESHWATER ECOSYSTEMS DOWNSTREAM FROM IRON MINES IN NORTHERN MINNESOTA

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We are using an integrative geochemical and molecular approach to characterize microbial communities associated with methylmercury (MeHg) production in freshwater sediments impacted by sulfate from mine water discharges on Minnesota's Iron Range. Prior research in the region has shown that MeHg does not accumulate significantly more rapidly in systems heavily impacted by sulfate, but the microbial processes responsible methylation in sulfate-impacted and sulfate-unimpacted ecosystems are presently unknown. Both methylation rates (enriched stable isotopes) and culture-independent techniques (hgcA gene and transcript sequencing, full-cycle rRNA methods, and metagenomics) were applied to the water column and sediment of two sulfate-impacted lakes in Northern Minnesota, and to sulfate-amended wetland sediment mesocosms.

Methylation rates and MeHg accumulation were not clearly related to sulfate concentration or sulfide accumulation in either the lakes or the sulfate-amended mesocosm sediment. In the lakes, hgcA gene cloning shows that while the potential methylating communities differ among the sites, more than 50% of the hgcA gene sequences at all locations are affiliated with the Geobacteraceae (Deltaproteobacteria), Methanomicrobia (Euryarchaeota), or unknown populations. hgcA transcripts affiliated with methanogenic Archaea, iron-reducing Deltaproteobacteria, and unknown populations indicate that these organisms in addition to sulfate reducers may be important contributors to methylmercury production in the least sulfate-impacted sediments studied. Metagenomic analysis, in progress, will be used to determine the taxonomy and metabolic potential of the unknown hgcA-expressing populations in the lakes.

In the sulfate-amended mesocosm sediment, methylmercury production rates vary over two orders of magnitude across the experiment but do not show a clear relationship with sulfate amendment level. Both MeHg and inorganic Hg increased in the overlying water of mesocosms with increasing sulfate amendment, though this increase was not related to an increase in MeHg or methylation potential in the sediment, and may be related to the influence of sulfide accumulation on Hg partitioning. Microbial diversity decreases with elevated sulfate concentration, but cell counts indicate approximately similar cell densities across all sulfate amendments. Based on 16S rRNA gene amplicon sequencing, certain groups of sulfate-reducing Deltaproteobacteria increase with increasing sulfate concentration, other sulfate-reducers show no change, and iron-reducers (Geobacteraceae) and methanogens (Methanomicrobia) decrease. We will also report hgcAB and dsrB amplicon libraries from across the experiment that will reveal relationships between the methylating communities and mercury biogeochemistry. These collective results expand our knowledge of the clades and environmental influences important for understanding mercury methylation in sulfate-impacted freshwater ecosystems.

TO-023

BIOGEOCHEMICAL CONTROLS ON MERCURY METHYLATION IN ALASKAN PEATLANDS SPANNING A LARGE RANGE OF TROPHIC STATUS

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Mercury (Hg) methylation is as a key area of research necessary to understand spatial and temporal variability of toxic methylmercury (MeHg) on the landscape. Numerous factors affect MeHg production, the most important being those that affect inorganic Hg(II) bioavailability (e.g., Hg(II) concentration and ligand composition), and those that affect microbial community composition and activity. The principal goal of this project is to decipher the relative importance of aqueous biogeochemistry versus microbial community on MeHg production in Alaskan peatlands exhibiting a range of trophic status, including those lacking electron acceptors that support the traditional respiratory pathway of MeHg production (e.g., sulfate reduction). MeHg production is carried out by different groups of microorganisms that possess the hgcAB gene cluster, including the well-studied sulfate- and iron-reducing bacteria (SRB and FeRB). However, less well known bacteria also possess the hgcAB genes, including: syntrophs, methanogens, acetogens, and fermenters. Field sites for this study (ombrotrophic bogs to mineral-rich fens) were purposely chosen to encounter this full range microbial community assemblage.

Our experimental approach employed intact peat cores, site porewater, and enriched isotopes of inorganic Hg(II) and MeHg tracers (198Hg and Me204Hg). The tracers were added to anoxic porewater from each site and allowed to equilibrate for four hours. Next, amended porewater solutions were injected into peat cores, held at room temperature for 24 hours and then frozen. In addition, several other well-known and characterized dissolved organic matter (DOM) solutions (two from the Florida Everglades, Williams Lake in Minnesota, and cysteine) that have been shown to increase bioavailability of inorganic Hg for methylation in pure culture, as well as a no-DOM control, were also equilibrated with the enriched Hg isotope solution and injected into peat cores. Our results show that ambient MeHg concentrations in peat and porewater are significantly greater (15-30x) in fens compared to bogs. Likewise, methylation rates using site-specific porewater were also greater at fen sites. Interestingly, however, when bog porewater containing the 198Hg tracer was injected into fen peat cores, a 3-5x increase in methylation rate was observed when compared to replicate cores injected with 198Hg amended fen porewater. Our overall results suggest that the intact microbial community is of paramount importance for controlling MeHg differences among wetland types. Paradoxically, bog water DOM serves to enhance the bioavailability of Hg(II) for methylation better than fen water, however, bogs are consistently the lowest MeHg containing sites.

TO-024

PLANT TRIMMING ON MICROBIAL HG METHYLATION IN A CHRONOSEQUENCE OF BOREAL WETLANDS

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Wetlands, which are anoxic and rich in organic matter, have been recognized as globally important sources of methylmercury (MeHg). MeHg can then be transferred to their hydrologically coupled lakes and streams, resulting in risk of human exposure to this potent neurotoxin. The formation of MeHg is mediated by different groups of anaerobic microorganisms. The main groups are believed to be sulfate-reducing bacteria (SRB), iron-reducing bacteria (FeRB) and methanogens. However, the specific roles of these different groups with regards to methylation in wetlands are incomplete and there is a paucity of data on distribution patterns, diversity and interactions. In this study, we explore biogeochemical processes controlling MeHg formation in a chronosequence of boreal wetlands, with a focus on the interaction between electron acceptors (e.g. sulfate), and electron donors in the form of labile carbon provided by vascular plants. The chronosequence was formed by post-glacial land uplift along the Bothnian Bay in northern Scandinavia. This has created a unique natural age gradient that spans around 4000 years within < 10 km, with large variations in catchment hydrogeochemistry and nutrient availability that alter the presence of electron acceptors under the same climatic conditions. For this purpose, we sampled 5 wetlands in each of three age groups. For each wetland, we subjected 5 sampling sites with samples collected at two soil depths to DNA- and RNA-based analyses to determine the combined microbial community composition, potential methylators and active methylators. To experimentally influence the electron donors, we trimmed vascular plants to see how a reduction in root exudates would impact the formation of MeHg and corresponding changes in microbial community composition. The older wetlands had the highest total mercury (THg) concentrations but also the lowest net MeHg production and ratio of (MeHg/THg), which is an indicator of net mercury methylation. The microbial analyses support the findings that the amount of Hg is not the main factor controlling net MeHg production, but rather the interplay between microbes and the availability of electron donors and acceptors.

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3e-3: Human exposure and health effects of mercury: epidemiology and population studies

TO-025

IS OCEAN FISH CONSUMPTION ASSOCIATED WITH CAUSING MERCURY TOXICITY OR PREVENTING IT?

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Selenium (Se), is an essential trace nutrient that is required for synthesis of selenocysteine, the 21st genetically encoded amino acid. Selenocysteine is required for the functions of ~25 genetically and functionally unique enzymes (selenoenzymes) that are expressed in human tissues; many with activities vital for brain function, health, and development. Mercury (Hg) is the only environmental insult known to cross placental and blood brain barriers and irreversibly inhibit selenoenzyme activities. Maternal exposures to methyl-Hg, (MeHg) can be especially harmful because MeHg can sequester Se in maternal tissues, thus limiting Se transport to the fetus. Studies indicate that the toxic effects of high MeHg exposures can be prevented by increasing dietary Se intakes, including those from eating Se-rich ocean fish. MeHg exposure from fish consumption is proportional to risk only in cases where MeHg concentration occurs in molar excess of selenium (Se). In this study, weanling male Long Evans rats were fed 0.2 µmol Se/kg diets for 5 weeks to deplete their Se body stores, making them highly dependent on dietary Se to support growth and brain selenoenzyme synthesis. Following the depletion period, rats were weighed and pseudo-randomly assigned to diets that contained either 0.2, 1.0, or 10 µmol Se/kg or similar amounts of Se from delipidated fish protein and were supplemented with either 0 or 40 µmol MeHg/kg and fed ab libitum for 5 weeks. During the course of the study, neurotoxicity was only noted in rats fed diets containing 0.2 µmol Se with 40 µmol MeHg. At the end of the study, brain Hg, Se, and selenoenzyme activities of thioredoxin reductase (TRx) glutathione peroxidase (GPx) were assessed along with F2-isoprostane (an indicator of oxidative damage). In animals with low dietary Se intakes, brain TRx and GPx activities were severely impaired by MeHg exposures, but increasing dietary Se from delipidated ocean fish protein increasingly counteracted the inhibitory effects of high MeHg exposures. Oxidative damage as indicated by F2-isoprostane concentrations in the brains of MeHg exposed rats was inversely related to brain GPx and TRx, strongly indicating that the oxidative damage known to be associated with high MeHg exposures is due to loss of selenoenzyme activities. This study found that dietary HBV is a superior index of risks due to high MeHg exposures. Because the HBV provides a direct reflection of the bimolecular reaction mechanisms associated with MeHg toxicity, it provides a more reliable approach to risk assessment than seafood safety criteria based on MeHg exposures alone.

TO-026

METALLOMIC QUANTIFYING METALS IN METALLOPROTEINS: THE LEVELS OF HG AND SE BINDING TO SERUM SELENOPROTEINS FROM METHYLMERCURY-POISONED RATS AFTER SE TREATMENT

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Metalloproteins - proteins containing metal atoms or clusters -, accounting for nearly half of all proteins in nature are involved in a wide range of important biological processes, like photosynthesis, respiration, water oxidation, molecular oxygen reduction, nitrogen fixation and metal homeostasis. Proteomic approach has been widely used in the characterization of metalloproteins, however, the in situ quantification of metals in metalloproteins remains a challenge. Metallomics is an emerging field addressing the role, uptake, transport and storage of trace metals in biological systems, which provides complementary tools for metalloproteomics.

It has been known for decades that selenium (Se) could antagonize the toxicity of mercury (Hg), both in inorganic (Hg2+) and organic (i.e. methylmercury, MeHg) forms in different organisms when co-exposed, but the mechanism underlying this antagonism is still not clear .It was proposed that selenite could react with Hg2+ in blood to form a Hg-Se-selenoprotein P (Sel P) complex, however, it is not known if such kind of complex will also form when selenite meet methylmercury (MeHg) in blood stream. Besides, it is not known how much Hg and Se in serum were bound to selenoproteins.

In this study, selenite was supplemented for 30 days in methylmercury-poisoned rats. Blood samples were collected and the contents of Se and Hg in serum were measured using inductively coupled plasma mass spectrometry (ICP-MS). Affinity chromatography (AF) coupled to ICP-MS was used to find out the Hg, Se binding selenoproteins in serum samples. Post-column isotope dilution analysis (IDA) using both enriched

78Se and 199Hg as spike was applied to quantify the levels of Hg and Se binding to selenoproteins. It was found that both Hg and Se were mainly bound to Sel P in serum in MeHg-poisoned rats after selenite treatment. Se promoted Hg to bind to Sel P in MeHg-poisoned rats, suggesting that Sel P plays an important role in fighting against the toxicity of MeHg.

TO-027

SELENIUM PROTECTS AGAINST TOXIC EFFECTS OF MERCURY ON CARDIOVASCULAR HEALTH AMONG INUIT IN CANADA

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Background: Selenium (Se) has been reported to protect against the neurotoxicity of mercury (Hg). However, the effect of Se against Hg on cardiovascular diseases remains unclear. Inuit living in the Arctic have high exposure to both Se and Hg through their marine mammal and fish rich traditional diet.

Objective: To characterize the co-exposure of Hg and Se among Inuit in Canada and to assess the interaction between Hg and Se exposure and its effect on cardiovascular health outcomes, such as stroke and hypertension.

Methods: Data was collected from the International Polar Year Inuit Health Survey (IHS) conducted in 2007 and 2008. Blood Se and Hg were measured, and self-report cardiovascular health outcomes were collected through a questionnaire interview from 2169 adults aged 18 and above.

Results: The mean age was 42.4 years, and 38.7% of the participants were male. The geometric means (GM) of blood Se and total Hg were 319.5 µg/L and 7.0 µg/L, respectively. The crude prevalence of heart attack, stroke and hypertension were 3.55%, 2.36%, and 24.47% respectively. Participants were categorized into 4 exposure groups according to blood Hg (high: ≥ 7.8 µg/L; low: < 7.8 µg/L), and Se (high: ≥ 280 µg/L; low: < 280 µg/L). The odds ratio (OR) of cardiovascular outcomes were estimated using general linearized models. Results showed the low Se and high Hg group had a higher prevalence of cardiovascular disease (OR=1.76 for hypertension, 1.57 for stroke, and 1.26 for myocardial infarction (MI)). However, the prevalence was decreased in both the high Se and low Hg group (OR=0.57 for hypertension, 0.44 for stroke, and 0.27 for MI) and the high Se and high Hg group (OR=1.14 for hypertension, 0.31 for stroke, and 0.80 for MI).

Conclusions: The high Se and low Hg group had the lowest prevalence of cardiovascular outcomes, except for stroke. These results suggest that Se exhibits a protective effect on cardiovascular disease through interaction with Hg.

TO-028

SELENIUM HEALTH BENEFIT VALUES ARE A MORE RELIABLE INDEX OF MERCURY ASSOCIATED RISKS

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Seafood safety evaluations regarding methylmercury (MeHg) are currently based on fish MeHg contents. Although this provides an accurate index of MeHg exposures, it fails to provide an accurate indication of risk. Studies of maternal MeHg exposures from eating certain types of highly predatory sharks or whales find subtle dose-dependent adverse effects on their children. However, studies involving consumption of typical varieties of ocean fish do not support the premise that maternal MeHg exposures result in adverse child outcomes. Instead, ocean fish consumption is directly associated with improved neurodevelopment. Exposures to MeHg has been found to be proportional to risk only in cases where MeHg concentration occurs in molar excess of selenium (Se) in the seafood consumed i.e., meats of highly predatory sharks or whales. Since MeHg is an irreversible inhibitor of Se-dependent enzymes (selenoenzymes), studies indicate that the toxic effects of high MeHg exposures can be prevented by increasing dietary Se, including Se-rich ocean fish. Selenoenzymes are normally present in all vertebrate cells, but are most important in brain and endocrine tissues where, among other functions, they prevent and reverse oxidative damage. However, these vital activities are lost when consumption of foods with disproportionately high MeHg contents transiently result in MeHg-dependent inhibition of selenoenzymes. The Se-Health Benefit Value (HBV) criterion is a predictive indicator of dose-effect relationships between MeHg and Se concentrations in the fish or seafood. Negative HBV's predict relative risks (e.g., pilot whale; -83) while consumption of increasing amounts of ocean fish with positive values (e.g., yellowfin tuna; 15.7 ±3.4) predict benefits. Epidemiological studies which report adverse outcomes in children have involved MeHg exposures from eating seafood's with negative HBV's. Although increasing ocean fish consumption increases maternal and fetal MeHg exposures, health benefits have been consistently observed when the seafoods have positive HBVs. Therefore, the HBV is a seafood safety indicator that reflects the beneficial nutrients provided by fish while allowing consideration of MeHg risks when present. Studies performed in-vitro, in cell culture and laboratory animal models, as well as epidemiological studies coincide in confirming that HBV-dependent predictions are superior to predictions based on MeHg exposures alone. Fish and background diets consumed by human populations can vary widely in Se content, and thus influence health outcomes observed in association with MeHg exposures. Epidemiological studies are likely to obtain more consistently reliable results if they consider dietary Se intakes as well as MeHg exposures in relation to health outcomes.

TO-029

CHRONIC EXPOSURE TO LOW-DOSE METHYLMERCURY (MEHG) INDUCES DIFFERENTIAL ACCUMULATION AND ASSOCIATED PROTEOME CHANGES IN DIFFERENT REGIONS OF MAMMALIAN BRAINS

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Human exposes to MeHg mainly through consumption of contaminated seafood. Paresthesia and numbness of the skin are some of the earliest syndromes of acute MeHg poisoning. As the MeHg load keeps increasing, other syndromes like dystaxia, dysarthria and visual impairment will follow. The sequential occurrence of pathological syndromes indicates that different regions of the brain respond differently to MeHg. In our previous study, we have observed that different amounts of Hg was loaded into different regions of the rat brain after chronic exposure to low dose of MeHg (40 μg/ kg bodyweight/ day) for 12 weeks. Comparative proteomic analysis revealed that there was a dramatic proteome changes in the somatosensory cortex upon chronic MeHg exposure. Proteins related to glycolysis, ATP production, neurotransmission, and protein synthesis were down-regulated in the somatosensory cortex, resulting in a metabolic deficit without observable abnormality phenotypically. In contrary to results obtained from the somatosensory cortex, we found different sets of differentially expressed proteins in the other regions. In the motor cortex, visual cortex and the cerebellum, some proteins involved in synaptic transmission and glycolysis (like synapsin and aldolase) were up-regulated. Beside rats, Hg loads and associated proteome changes in brain tissues from other top marine consumers including ringed seals and polar bears were also examined. In general, proteins related to glycolysis, ATP production, and neurotransmission showed differential expressions upon chronic MeHg exposure. Interestingly, only a small fraction of the proteomes was affected in the frontal and occipital lobe of polar bear while relatively more proteins showed differential expressions in polar bear cerebellum. In ringed seals, differences in proteome changes across frontal lobe, occipital lobe and cerebellum were also observed. Based on the current findings, neurotransmission, glycolysis and other metabolism involved in energy production in mammalian brains were primarily affected by chronic MeHg exposure. From our results, it is also obvious that different regions of the brain showed different proteome changes and this may account for the sequential occurrence of different pathological syndromes in human suffered from acute and increasing MeHg loads.

TO-030

MERCURY AND THE IMMUNE SYSTEM: WHAT IS THE CONTRIBUTION OF IMMUNOTOXIC MECHANISMS TO MERCURY TOXICITY

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Mercury compounds, including elemental (Hg°), inorganic (iHg), and organic forms (including alkyl, methyl, and ethyl Hg), have effects on the immune system as demonstrated in experimental, cellular, ecotoxicological and epidemiological studies. However, the role of immunotoxicity in the major health outcomes associated with exposures to these mercury compounds is at present unclear. Inconsistencies among studies may have reduced attention to this question. However, the lack of concordance may be due to the importance of interactions between mercury compounds and other risk factors in eliciting these adverse outcomes. For example, suppression of primary immune responses may be manifest in populations exposed to an infectious pathogen or vaccination; induction of autoimmune responses may be manifest in populations exposed to an unrelated triggering event such as a virus; neurotoxicity may involve viral infection or other pyrogens. Under these conditions, serious clinical outcomes may be observed, including increased morbidity and recurrence of malaria; failure of HBV vaccinations; greater severity of autoimmune myocarditis; and structural disruption of neurodevelopmental programming.

This model suggests that mercury may be a necessary but not sufficient risk factor for outcomes involving immunotoxicity and other stressors This hypothesis has implications for both mechanistic models and the design of epidemiological and ecotoxicological studies since the observation of adverse effects may depend in most but not all cases on mercury exposure and concurrent infections or immunosuppressive medications, the host immunogenome, sexual dimorphism of immune function, all of which are likely to be important modifiers of risk and outcome.

TO-031

FACTORS AFFECTING MERCURY EXPOSURE FROM FISH

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Studies of mercury in blood and hair provide a direct assessment of mercury exposure and are often linked with estimates of fish consumption frequency. These studies provide a basis to compare estimates of mercury intake based on fish consumption rates and mercury concentrations; however, estimates of fish consumption rates are difficult to measure and are highly variable. Estimates of mercury exposure also should consider ratios of total mercury (THg) to methylmercury (meHg), bioavailability of fish mercury, and impacts of cooking on fish concentrations. Studies conducted around the world in the past ten years provide a basis for assessing fish consumption-based risk estimates. In some cases biomarker data indicated exposures much less than predicted, suggesting lower than assumed fish consumption, fish mercury concentrations, mercury bioavailability, or a combination of factors. MeHg concentrations typically are predicted based on THg concentrations. United States Environmental Protection Agency (USEPA), Health Canada and the European Food Safety Authority apply a factor of 1.0-0.95 (unitless) to convert total mercury levels in fish tissue samples into meHg levels, but our compilation of recent studies indicates a range of 61-85% may be more representative. Mercury concentrations are expected to increase during cooking because mercury is concentrated in muscle rather than in water and fat that may be lost during cooking. Recently, USEPA applied an adjustment factor of 1.5 to mercury concentrations in raw fish when estimating mercury doses from cooked fish portions. Recent studies suggest that while high heat cooking methods such at grilling result in cooking factors of 1.4-1.5, lower heat methods such as steaming, roasting or frying fish result in little or no increase in mercury concentrations. Recent studies also indicate that mercury absorption from fish meals may be much lower than the 95% assumed by North American and European regulatory authorities, especially when testing cooked fish. The practical impact of these factors is that larger amounts of fish may be safely consumed than currently is assumed. For example, for raw fish with 0.3 ug/g THg, the default assumptions (THg:meHg = 0.95, cooking factor = 1.5, bioavailability = 95%) lead to a conclusion that 2.5 meal/month may be safely consumed, whereas reasonable alternate assumptions (THg:meHg = 0.8, cooking factor = 1.3, bioavailability = 80%) yield an estimate that it is safe to consume 4 meals/month. Considering the nutritional benefits of fish consumption, understanding the reliability of such estimates is critical to providing appropriate guidance to fish consumers.

TO-032

MITIGATING THE HUMAN HEALTH IMPACTS OF HYDROELECTRIC DEVELOPMENT IN CANADA

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Developing hydroelectric plants in circumpolar regions is a part of the energy strategy of many northern countries; in Canada alone there are multiple existing plants and 22 facilities are currently under construction or are planned to be built. Flooding, including the flooding associated with hydroelectric developments, has been shown to increase microbial production of methylmercury (MeHg), a known neurotoxin which bioaccumulates in country foods (e.g. fish) and the humans and wildlife (e.g. marine mammals) who consume them. Most of these existing, new or planned hydrolectric projects are located in the vicinity of indigenous communities, who are frequent consumers of country foods, including fish. Health Canada has established its tolerable daily intakes (TDI) for methylmercury at 0.2 ug/kg bw per day for children and women of childbearing age and at 0.47 ug/kg bw per day for the general population. Analysis of human samples (usually hair or blood) can provide information on baseline MeHg levels in indigenous communities, which in some cases are already elevated. Consumption surveys allow for estimation of daily intakes and development of consumption advisories, but due to the inherent uncertainty in these surveys, they may not be the most effective tool in limiting exposure to MeHg. In order to provide meaningful advice on the safety of consuming country foods (fish and marine mammals) from these reservoirs and adjacent water bodies further study in the area of MeHg production and transfer in newly flooded areas is needed, in addition to more information on the short-term toxicokinetics of MeHg. This presentation studies the ways MeHg intake is currently being mitigated, explores the new research being done in the area of MeHg mitigation, and examines the risks and benefits of country foods consumption by indigenous communities in Canada and elsewhere.

3f: Methylmercury toxicokinetics and toxicodynamics: human and animal models

TO-033

PRINCIPLES, PRACTICE AND PRESSING QUESTIONS OF METHYLMERCURY TOXICOKINETICS AND TOXICODYNAMICS IN HUMANS AND ANIMAL MODELS

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The fate of mercury in the body after an environmental exposure to methylmercury (MeHg) is dictated by fundamental principles of toxicokinetics. Understanding the potential impact of MeHg toxicity therefore requires a working knowledge of the characteristics of adsorption, distribution, metabolism and excretion. In addition, understanding MeHg toxicity at relevant sites of action, such as in the fetus and the brain, requires insight into toxicodynamic interactions with tissue specific factors and nutrients in various compartments of the body. The extent of variation in toxicokinetic traits, such as elimination rate, which dictates the MeHg half-life (t1/2), is incompletely characterized in both humans and animal models. For example, methylmercury half-life in humans is reported to range from t1/2 ~ 30 to >120 days, yet underlying factors controlling this variation are not known. Furthermore, recent evidence from our own studies demonstrates that elimination rate can vary within an individual over time. A working knowledge of toxicokinetics and toxicodynamics is even more essential for interpreting complex studies on the genetic, environmental and nutritional factors that modify methylmercury toxicity as well as for characterizing the variety of environmental sources of MeHg exposure. This presentation aims provide a condensed summary of the toxicokinetic and toxicodynamic principles specific to MeHg. Examples of representative studies of half-life determination in human and animal models will be presented to illustrate both past and emerging methodologies and to highlight examples of toxicokinetic parameters currently used for regulatory guidelines of MeHg exposure. How toxicokinetics and toxicodynamics are applicable to interpreting MeHg exposures in individuals and populations, with particular attention to fetal and early life exposures, will be outlined. Finally, gaps in understanding methylmercury toxicokinetics and toxicodynamics will be laid out to enhance the discussion of the way forward in this fundamental area of mercury research.

TO-034

METHYLMERCURY VERSUS SELENIUM, VITAMIN E, AND DOCOSAHEXAENOIC ACID IN FETAL CIRCULATION: COMPARISON WITH MATERNAL STATUS

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Methylmercury (MeHg) is a neurotoxicant that the developing brain of a fetus is especially susceptible to. On the other hand, selenium, vitamin E (VE), and docosahexaenoic acid (DHA) have been reported to protect MeHg toxicity. The placenta strongly controls the biochemical composition of the fetal circulation by regulating entry of nutrients derived from the mother. Therefore, the study of the characteristics of the profiles of mercury in fetal circulation as well as those of selenium, VE, and DHA, potential protective factors against the toxicity of MeHg, are important to evaluate the high susceptibility of the fetus. The objectives of this study were to: 1) investigate the characteristic of the placental transfer of nutrients and MeHg by comparing biochemical composition in the fetal and maternal blood and 2) investigate the difference of the status of Hg relative to Se, VE, and DHA in fetal blood versus maternal blood to estimate the sensitivity of the fetus to MeHg toxicity. Blood samples were collected separately from the maternal and umbilical vein at parturition from 54 mother-infant pairs of Japanese. The characteristics of fetal circulation were low contents of lipid components and fatty acids and high contents of amino acids, including methionine, compared with those in maternal circulation. Mercury in cord blood (7.26 ng/g) was higher than in maternal blood (185%). Selenium in cord blood (153 ng/g) was similar to maternal blood. On the other hand, VE (0.31 mg/dl) and DHA (57.9μg/ml) in cord blood were lower than maternal blood (45% for VE and 22% for DHA). These results showed that the ratios of selenium/mercury, DHA/mercury, and VE/mercury were lower in fetal circulation than those in maternal blood. Not only the approximately two times higher Hg but also the lower ratios of protective factors such as selenium, VE and DHA against mercury in fetal circulation may contribute to the high susceptibility of a fetus to MeHg toxicity.

TO-035

BIOAVAILABILITY OF METHYLMERCURY FROM COMMONLY CONSUMED SEAFOOD: AN IN VITRO INVESTIGATION OF GASTROINTESTINAL AND COLONIC DIGESTION

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Seafood provides essential nutrients, but is also contaminated with methylmercury (MeHg). Current risk assessments for ingested MeHg assumes it is 100% bioavailable in the human gastrointestinal tract. However, recent studies on MeHg bioavailability suggest otherwise. These studies were mostly performed outside of North America, on seafood not commonly consumed in North America, and focus almost exclusively on bioaccessibility (digestive processes) rather than bioavailability (cumulative digestive + absorptive processes). We aimed to evaluate both MeHg bioaccessibility and bioavailability from edible tissue of the top 10 most consumed types of seafood in the United States, identified by a previous survey; as well as assess the role of the colon in MeHg bioaccessibility and bioavailability. We used an in vitro model of human digestion including gastric and small intestinal phases; some digestions also included a colonic phase. Bioaccessible MeHg was measured in the soluble fraction resulting from these digestions. Soluble fraction was added to a Caco-2 Transwell assay to assess MeHg bioavailability. After gastrointestinal digestion, mean MeHg concentrations ranged from 0.73 ng/g (scallop) to 527 ng/g (canned white tuna) in undigested seafood, from 0.73 ng/g (scallop) to 366 ng/g (fresh tuna) in bioaccessible fraction, and from 0.34 ng/g (scallop) to 266 ng/g (fresh tuna) in bioavailable fraction. MeHg bioaccessibility ranged from 50% (canned white tuna) to 100% (shrimp, scallop), and bioavailability from 29% (crab) to 67% (salmon). In preliminary studies, colonic digestion of fresh tuna reduced MeHg bioaccessibility by 88% relative to gastrointestinal digestion only; colonic digestions conducted at pH 5.7 had 60% less bioaccessible MeHg than digestions conducted at pH 6.4. In conclusion, both digestive and absorptive processes seem to have a role in reduced MeHg bioavailability, thus suggesting that ingested MeHg is less than 100% bioavailable. More accurate estimates of MeHg bioavailability can help properly balance the toxicological risks and the nutritional benefits of consuming seafood, though additional research is needed before use in risk assessment.

TO-036

MERCURY TRANSFER ACROSS THE HUMAN PLACENTA: FROM KINETICS TO GENETICS

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Mercury is well known to cross the placenta, to accumulate in placental tissue, and to pass onto fetal blood and fetal organs. An active transport across the placenta has been assumed. The underlying mechanisms however were virtually unknown. The genetic factors modulating placental toxicokinetics remain unclear just as well. The placenta is a unique organ. The tissue phenotype, i.e., placental protein level and function, can easily be determined. The term placenta is non-invasively available and, in addition, primary cells can be isolated therefrom.

In a recent project on mercury toxicokinetics in healthy human term placentas, candidate proteins putatively involved in mercury uptake, metabolisation and efflux were examined. Expression, localization and function of overall 27 proteins were determined in human primary trophoblast cells and the trophoblast-derived choriocarcinoma cell line BeWo. To prove involvement of the proteins in placental mercury metabolism, we used small interfering RNA (siRNA) and exposed cells to methylmercury. Localization of the proteins in human term placenta sections was determined via immunofluorescence microscopy.

We found two amino acid transporter subunits (LAT1, rBAT) and one ABC transporter (MRP1) to be involved in mercury toxicokinetics of trophoblast cells. According to our data, a model could be deduced which can explain why mercury is efficiently transported towards the fetal side: It uses LAT1 (probably also LAT2) and rBAT dimerized to another light chain than b0,+ at the apical side of the syncytiotrophoblastto enter trophoblast cells. Intracellular mercury dissociates from cysteine, binds to glutathioneand is therefore no longer a substrate of amino acid transporters. Mercury conjugated to glutathione is effluxed by MRP1. We made further important observations. Human trophoblast cells show strong variation in mercury accumulation capacity and in protein expression levels. It is reasonable that abundance and activity of the involved transporters determine mercury transfer rates across the syncytiotrophoblast. This raises the question on the regulatory factors behind. In our search on genetic markers, we found some evidence for sequence variants including one ABCC1 polymorphism to be related to placental mercury toxicokinetics.

TO-037

UNCOVERING THE GUT MICROBIOME MACHINERY BEHIND MERCURY TRANSFORMATION

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Fish is an important source of nutrients essential for functions including brain growth and development. However, contaminants such as methylmercury (MeHg) bioaccumulate in fish, and biomagnify along the food chain resulting in higher concentrations among predatory fish. Due to increasing anthropogenic activities, mercury (Hg) has been remobilized in the environment leading to increases in fish Hg concentrations. Epidemiological studies show great variation in Hg uptake between different human populations but also between individuals within a population. Although, the genetic makeup of an individual plays a role in this variation, the gut microbiota of individuals can also play an essential role in the transformation of Hg. Study of the gut microbiome is a growing field of research that has shown links between the gut microbiota to its hosts physiology, endocrinology and its immune system. Numerous studies have shown link between GI functions and gut microbial community structure including its ability to demethylate MeHg. However, little is known about the roles of gut microorganisms, if any, on mercury transformations. Our goal is to test the hypotheses that certain taxa of bacteria are responsible for MeHg transformations and components of the diet can mediate shifts in gut microbiome that can affect MeHg transformations. Using a series of batch experiments, we evaluated the effects of diet (by altering relative abundances of carbohydrate, fiber, lipid, or protein) on the gut microbial community structure of several individuals. We tracked mercury methylation and demethylation rates for each diet and conducted high throughput sequencing of the 16S rRNA gene fragments to determine microbial community structure. For one individual, we observed 100% decrease in MeHg concentration in a protein-rich medium. Our data suggest that two selected taxa could be responsible for microbial mediated mercury demethylation in the gut environment. Both have not been reported to have mercury demethylation capabilities and the mechanism remains unknown. This study is an important first step in understanding the mechanism behind mercury transformation in the gut microbiome.

TO-038

MERCURY SPECIATION AND SUBCELLULAR DISTRIBUTION IN EXPERIMENTALLY-DOSED AND WILD BIRDS

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Many bird species are exposed to methylmercury (MeHg) at levels shown to cause sub-lethal effects, including impaired physiology, behavior, and reproduction. However, the risk for negative health effects of MeHg can vary among species and with age. Birds can assimilate dietary MeHg in liver tissues, however, considerable variability in concentrations has been observed among species and individuals. Differences in MeHg toxicokinetics may play a role in the variability observed in MeHg assimilation and risk. Recent studies investigating how metals are distributed at a subcellular level have categorized subcellular fractions into metal-sensitive fractions: heat-denatured proteins (HDP), mitochondria, and microsomes and lysosomes, and detoxified metal fractions: heat-stable proteins (HSP) and granule-like fraction. A greater proportion of Hg located in metal-sensitive fractions may indicate an increased health risk. The objective of this study was to increase the understanding of MeHg toxicokinetics in birds by determining liver mercury (Hg) speciation and subcellular distribution in two avian species and across developmental time points. We used MeHg egg injection of a model avian species, White Leghorn Chicken (Gallus domesticus), to investigate liver Hg speciation and subcellular distribution among day 19 embryos, and day 1 and 7 hatchlings. We compared these results with those from maternally deposited Hg in wild embryonic Ring-billed Gulls (Larus delawarensis). THg in liver was mostly MeHg for all species and time points, indicating little MeHg demethylation in embryos and hatchlings. THg concentrations in chicken livers ranged from 1.8 – 11.8 µg/g dw, with lower concentrations seen in embryos. Embryonic Ring-billed Gull liver tissues had much lower THg concentrations, from 0.08 – 0.17 µg/g dw. Chicken and Ring-billed Gull liver tissues were also subjected to a subcellular partitioning procedure using differential centrifugation, NaOH digestion, and heat denaturation. Subcellular fractions were analyzed for THg and the proportion of Hg in each fraction was determined, relative to the total Hg burden. The proportion of Hg in subcellular fractions differed little among time points for chicken liver, with embryos having lower Hg in HSP. Subcellular distribution also differed little between embryonic chicken and Ring-billed Gulls, with gulls having greater Hg in HSP. All species and time points had a greater proportion of Hg in the metal-sensitive fractions, with HDP and mitochondria proportions combined ranging from 58.8 – 61.7%. These results indicate an increased health risk from MeHg exposure in embryos and hatchings. This study can improve understanding of MeHg toxicokinetics and how it relates to MeHg sensitivity in birds.

TO-039

VARIABILITY IN METHYLMERCURY (MEHG) METABOLISM, ELIMINATION RATE, AND GUT MICROBIOME COMPOSITION IN HUMANS FOLLOWING FISH CONSUMPTION, THE MEHG METABOLISM AND ELIMINATION STATUS (MERMES) STUDY.

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Concern about methylmercury (MeHg) exposure has resulted in fish consumption advisories. These advisories have been controversial and difficult to establish because of the highly variable outcomes of MeHg exposure seen across populations as well as between individuals. This variability may be due to individual and population differences in MeHg metabolism. In the human body, elimination of mercury (Hg) stemming from a MeHg exposure occurs slowly (kel ~ 0.01 day-1 or t1/2 ~70 days) and thus is a major determinant of the Hg body burden. Human MeHg elimination, as determined by a variety of methods, is highly variable ranging from t1/2=35 to >150 days. The mechanisms that control MeHg toxicokinetics in the human body remain poorly understood. Nonetheless, microbial demethylation of MeHg in the lumen of the gut is thought to play a role by producing inorganic Hg (I-Hg) that is readily excreted in feces. To shed light on the biological determinants controlling MeHg body burden we have examined MeHg elimination and metabolism in a cohort of 40 subjects. Subjects ate three tuna fish meals, each one week apart, followed by a 60-day elimination period where no fish or seafood was consumed. Longitudinal analysis of hair (collected on day 60) was performed for 202Hg and 34S by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to derive hair growth rate and determine Hg elimination rates. Fecal samples collected during the elimination period were analyzed for %I-Hg as a proxy for MeHg demethylation. Elimination rates were found to vary more than two-fold ranging from kel=0.0246-0.0103 day-1 (estimated t1/2= 28.2-67.3 days). The method also proved sensitive in detecting Hg exposures occurring prior to the fish meals. Across all subjects, faster elimination rates were seen to positively associate with the %I-Hg in feces, consistent with the notion that demethylation plays a role in MeHg metabolism and excretion. In parallel with our elimination studies, we sampled feces of our participants before and twice after tuna consumption for gut microbiome characterization. Bacterial abundance and diversity was determined via 16S rRNA sequencing and phylogenetic analysis. A pattern of differential abundance over the course of the fish meals can be seen in select taxa. Preliminary analyses, across the subjects showed select taxa associated with faster Hg eliminators than in the slower eliminators. Our results highlight the existence of individual variation in MeHg metabolism and elimination and point to a central role for MeHg demethylation in this variation. (NIEHS P30ES001247, R21ES024859).

TO-040

TOXICOKINETICS OF METHYLMERCURY IN NORTH ATLANTIC PILOT WHALES (GLOBICEPHALA MELAS)

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Methylmercury (MeHg) is a neurotoxin that biomagnifies in food chains. High levels of MeHg have been observed in both marine mammals and humans. Although the adverse health effects of MeHg are well-documented, the toxicokinetics of MeHg in mammals are not as well understood. The main objective of this study is to better understand MeHg metabolism in long-finned pilot whales (Globicephala melas). To do this, we constructed a toxicokinetic model parameterized by analytical measurements of total Hg, MeHg and stable Hg isotope in various organs (brain, heart, kidney, liver, muscle, placenta, and spleen) from seven individuals. We also investigated how physical characteristics like age, sex, and length affect metabolism. Results show the liver had the highest total mercury and MeHg concentrations (adult mean total Hg = 146.5 mg/g ww, MeHg = 7.3 mg/g ww) but also the lowest fraction of MeHg (adult mean percentage = 5.4%). The highest percentages of MeHg were found in the heart and muscle. Additionally, estimated age (range: 2-32 years) is strongly positively correlated with several organs total mercury concentration (R2 = 0.84 for brain, 0.58 for heart, 0.83 for kidney, 0.85 for liver, 0.79 for muscle) and MeHg concentrations (R2 = 0.71 for liver, 0.62 for muscle). The fraction of methylmercury, however, significantly decreases with age for brain (R2 = 0.91), heart (R2 = 0.61), kidney (R2 = 0.58), and liver (R2 = 0.61), suggesting that whales demethylation capability may improve with growth. Stable Hg isotope measurements in each organ will be presented to enhance understanding of potential mechanisms affecting metabolism and variability of in situ demethylation among whale individuals. The findings of this study will extend our understanding of how metabolism alters the internal body burden of MeHg and will shed light on sources of currently unexplained MeHg variability observed in marine mammals and human populations.

4a-1: Informing the implementation of the Minamata Convention: the role of scientific assessments

TO-041

UNEP GLOBAL MERCURY ASSESSMENT 2018

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UNEPs Governing Council has charged UNEP with updating its 2013 Global Mercury Assessment (GMA) within a period of 6 years, i.e. for delivery no later than 2019.

Methods for estimating global emission and release inventories will be similar to those employed in the GMA 2013 inventory prepared by UNEP/AMAP for the year 2010 with new work with respect to quantification of releases of mercury to the aquatic environment. Environmental fate, transport and occurrence will be summarised based on existing knowledge, models and databases. The technical background report will be structured around the following 5 components:

Updating the inventory of global emissions of mercury to air from anthropogenic sources in 2015. This component will include the development of updated global and country level estimates using a methodology similar to that employed in the GMA 2013. Work will be undertaken to improve the basis for the estimates through a review of new information i.e. activity data, new emission control technologies, new data on mercury consumption. New sectors will be addressed where relevant.

Development of estimates of releases of mercury to the aquatic environment from anthropogenic sources (target year 2015). The GMA 2018 will attempt to compile a comprehensive global inventory of releases of mercury to water from anthropogenic sources by using methods adopted from the UNEP Toolkit complemented with other studies and inventories.

Updating information on modelling of atmospheric transport of mercury from source to receptor regions. Modelling of long-range atmospheric transport of mercury will be updated to incorporate new information and results from additional/improved models. Focus of the work will be on global source-receptor modelling results. Results of regional modelling will also be reviewed with respect to recent modelling developments.

Updating information on mercury transport and fate in aquatic environments. Current knowledge on aquatic cycling of mercury will be updated to incorporate new information and results from relevant models, including evaluation of mercury contributions from anthropogenic vs. natural sources.

Updating information on environmental levels and trends of mercury in air, biota and humans. Observations of mercury in air will be updated to incorporate new information. New sections covering levels and trends of mercury in (aquatic) biota and in humans will be included in this assessment. Biota sections will prioritise species that are important indicators of contamination, sources of exposure to humans (e.g. consumed fish species) or species potentially affected by mercury contamination (e.g., fish feeding birds).

TO-042

THE GEO FLAGSHIP ON GLOBAL OBSERVING SYSTEM FOR MERCURY (GOS4M) IN SUPPORTING THE IMPLEMENTATION OF THE MINAMATA CONVENTION

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A first attempt to develop a global observing system for mercury was carried out within the GMOS (Global Mercury Observation System) project (www.gmos.eu). For the next decade GMOS will continue its activity as part of the GEO (2016-2025) Strategic Plan and its GEO Flagship Global Observing System for Mercury (GOS4M). GOS4M will continue, like GMOS, to support the achievement of goals and objectives of the UNEP Fate Transport Partnership Area, that among others, include the support to nations in the implementation of the Minamata Convention. Main objectives of GOS4M are to: (i) invite existing mercury monitoring networks i.e., GMOS, NADP, Asia Pacific Mercury Monitoring Network, AMAP, EMEP, Environment Canada Network, GBMS, to cooperate and elaborate a shared vision and the future governance of a worldwide observing system for mercury that would involve representatives of governments, monitoring networks, NGOs and UNEP; (ii) increase the availability and quality of Earth Observation data and information to track mercury releases and anticipate changes in the global environment; (iii) support harmonized metadata production, archiving and sharing within the mercury network; (iv) develop advanced web services for using and discovering information from metadata and data coherent with GEO Sharing Principles in cooperation with nations and UNEP in support of the policy mandate through the Minamata Convention. Therefore the aim of this oral presentation is to highlight major initiatives and actions already in place in the framework of GEO Strategic Plan (2016-2025) and UNEP FT to support nations and UNEP in the implementation of the MC.

TO-043

WHY UNDERSTANDING THE CHEMICAL COMPOSITION OF GASEOUS OXIDIZED HG IS IMPORTANT FOR GLOBAL AIR POLLUTION POLICY

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Recent work has demonstrated that the chemical compounds of gaseous oxidized mercury (GOM) can vary across space and time, and concentrations may be 2-to-13 times higher than previously thought. In addition, due to lack of capture by the instrument currently applied in networks worldwide, and data from this instrument being used in models, dry deposition of GOM is underestimated. GOM collected using cation exchange membranes and nylon membranes provide evidence for this. This has significant implications for ecosystem and human health. Trajectory analyses and chemistry measured by thermal desorption analyses indicate that GOM chemistry is dependent on oxidants in the air. Thus, chemistry of GOM is intricately linked with oxidant chemistry that is impacted by humans in the planetary boundary layer and free troposphere. The different GOM compounds that have been identified include: HgBr2, HgCl2, HgO, Hg-nitrogen and sulfur compounds, 2 unknown compounds with clear peaks, and organic compounds.These different GOM compounds will have different deposition velocities, chemistry, and potential bioavailability. Data developed demonstrate that a variety of compounds can be produced in areas with mobile sources and the potential for organic compounds cannot be ruled out. Thus, deposition in cities and areas associated with high density of mobile sources may be exacerbated. This new information is important when considering implementation of the Minimata Convention. Any atom of elemental mercury (Hgo) that is emitted can be converted to GOM. Thus, reduction of emissions will facilitate reduction of production of GOM. In addition, it is important to consider that reduction of air pollution (atmospheric oxidants) will also reduce GOM deposition. Lastly, since coal combustion is a significant source of mercury, carbon, and oxidants, and these all impact everyone across the globe, management of Hg can also be done through management of interrelated gases.

TO-044

ANTHROPOGENIC MERCURY IN RUSSIA: INVENTORY OF RELEASES, EMISSION TESTS, PRIORITIES FOR FURTHER ACTION

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Development of comprehensive up-to-date inventories of mercury (Hg) releases at national and regional levels is needed to deepen the understanding of the global anthropogenic Hg cycle and to ensure effective measures under multilateral environmental agreements, primarily the Minamata Convention on Mercury. This paper describes the development of national inventory of anthropogenic Hg releases for the Russian Federation. Combination of various data and information sources, including Russian national statistics on activity rates, national industry reports, as well as previous national and international studies are used to estimate Hg releases into air, water and land. The inventory methodology is based on the 2015 edition of UN Environment-developed Toolkit for Identification and Quantification of Mercury. With respect to Hg emissions into the air, various emission factors, developed both domestically and internationally are used. Results of Hg emission tests performed at non-ferrous and cement plants in the Russian Federation complement the estimates of releases derived from application of the UN Environment methodology. Total anthropogenic releases of Hg in the Russian Federation are estimated to have been around 1.49 Gg in 2012. Releases into land contribute the largest fraction of 49% to the total releases of Hg in the country. These releases, however, are rather localized around major mining sites in the Asian part of Russia. The second largest fraction of releases belongs to the general waste category with about 19%. By-product and impurities category generates some 15% of releases. Emissions to air, as one of the key source of the global Hg transport are estimated to contribute some 6% to the total national Hg releases only. Primary metals production and energy generation are identified to be the main sources of emissions, with the energy generation sector leading in Hg emissions to air, and the primary metals production leading in Hg releases to land. Hg release hotspots are mainly located in historically industrialized areas on the Ural Mountains region, East and West Siberia, and South European part of Russia. Some heavily Hg-polluted territories from the past industrial activities and related mainly to chlorine production are also identified in the study. The study results suggest the need for the development of further environmental policies and regulations in the Russian Federation to effectively manage Hg releases pollution. The study is carried out within the joint UNEP-Global Environment Facility project Pilot Project on the Development of Mercury Inventory in the Russian Federation (GFL-2310-2760-4C83).

TO-045

THE POTENTIAL ROLE OF PASSIVE AIR SAMPLING IN THE IMPLEMENTATION AND EFFECTIVENESS EVALUATION OF THE MINAMATA CONVENTION

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Implementing and evaluating the effectiveness of the Minamata Convention requires the (1) identification and characterization of mercury sources to the atmosphere, (2) the long term monitoring of mercury in the vicinity of identified sources to assess effectiveness of local efforts to reduce emission to the atmosphere, and (3) long term monitoring at background sites to assess effectiveness of regional and global efforts to reduce emissions. The case will be made that passive sampling techniques for gaseous mercury in the atmosphere have now matured to the point, where they can play an important role in meeting all three of these requirements. Air concentrations are directly related to atmospheric emission rates and thus are most suitable for locating emissions spatially and tracking emissions temporally. While active air sampling techniques are well established and can reliably provide mercury concentrations at very high temporal resolution, they are expensive and require electrical power and trained operators. Passive air samplers are cheap, simple to deploy and require no power and therefore are most suited for recording spatial concentration variability. The primary limitations of passive air samplers do not affect their usefulness for meeting the three requirements. First, time-weighted average concentrations over extended periods of time are required for implementation and effectiveness evaluation, i.e. in most cases high temporal resolution is not necessary. Second, even if passive sampling accuracy may not (yet) be as high as for pumped samplers, it is mostly relative air concentration differences in space and time that are useful in implementation and effectiveness evaluation. Passive air samplers can be as accurate as active samplers in recording mercury concentration differences in space and in time. The talk will draw on experiences in using passive air sampler in (1) the effectiveness evaluation of the Stockholm Convention for Persistent Organic Pollutants and (2) in mercury source identification and characterization.

TO-046

EVALUATING RELEASES OF MERCURY TO AQUATIC ENVIRONMENTS FOR MEETING NEEDS OF THE MINAMATA CONVENTION – GLOBAL PERSPECTIVE

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Control and reduction of mercury releases of aquatic systems are specific priorities addressed by the Minamata Convention. According to Article 9 of the Convention, each Party shall establish inventory of releases from relevant sources, and the Conference of the Parties shall adopt guidance on the methodology for preparing such inventories. However, there are no general or agreed upon approaches or methodologies that would serve this purpose. Moreover, in contrast to atmospheric emissions, aquatic Hg releases are greatly understudied. On a global scale, UNEP/AMAP Global Mercury Assessment (GMA) 2013 was the first attempt to compile a global inventory of such releases. However, this first inventory had large associated uncertainties. In this contribution, we will present an updated version of the inventory prepared for the GMA 2018, building on most recent information available and including new previously unaccounted for source categories. We will discuss data availability and methods used to estimate the releases. We will compare global estimates in the light of different assumptions and approaches used. The main focus will be on sectors of relevance for the Minamata Convention. Developed inventory estimates will be compared with available nationally reported releases estimates, independent databases/registers and other literature sources using different assumptions and approaches. Major components of uncertainties and their parametrization will also be addressed, as well as regional differences resulting from differences in environmental regulations and control technologies.

TO-047

HOLISTIC PERSPECTIVE IS NEEDED TO ENSURE SUCCESS OF MINAMATA CONVENTION ON MERCURY

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The Minamata Convention on Mercury (MC) will enter into force soon after 50 countries have ratified the MC. Many of the parties of MC are now developing their National Implementation Plans (NIP) which focus on fulfilling the obligations defined by the articles of MC. However, we found that there is an important weak point in the structure of MC which overlooked the inter-connections of articles. Like most international conventions, MC is organized by different articles. However, the obligation strength for the different articles are different. Some of the articles, for example, Article 12 on contaminated sites, are rather soft, the parties are only encouraged to take certain actions, and no firm obligations are defined. There is therefore a potential risk that Hg may shift from articles with firm obligations to articles with soft obligations. Since no mandatory actions are required, Hg pollution is not reduced from a holistic point of view. Furthermore, in the articles with firm obligations, no attention is paid to the processes after Hg is removed. Hg exists as impurities in either wastes or by-products. In many countries, the generated wastes will be utilized in order to minimize the volume of solid waste. This will cause secondary emission of Hg from waste/by-product utilization processes. Typical example is desulfurization gypsum from coal fired power plants will be used as building materials which may cause significant re-emission of Hg to air.

Based on our studies on the holistic Hg material flow, we identified two issues what need to be addressed in a timely manner. First, the parties should do a thorough survey of flows of Hg after Hg is removed from one sector (corresponding to one MC article). Secondly, holistic management measures should be taken to avoid Hg shifting from firm articles to soft articles.

TO-048

UNIDO CASE STUDY IN MONGOLIA: REDUCE EXPOSURE OF MERCURY ON HUMAN HEALTH AND THE ENVIRONMENT BY PROMOTING SOUND CHEMICAL MANAGEMENT

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This technical cooperation project funded by the Global Environment Facility (GEF) was designed to strengthen national and local capacity to effectively manage and reduce mercury emissions. Despite existing political will, the government of Mongolia did not have the full resources or the capacity to effectively manage mercury containing waste as well as historical mercury contamination hot-spots. In the case of the Boroo site in the Selenge province, the soil, sediment, water (surface and groundwater) and vegetation containing mercury are considered as mercury containing waste.

The project was executed in partnership with the Ministry of Environment, Green Development and Tourism, the Ministry of Health and the Mine Reclamation Corporation (Mireco) of Korea, and a consortium led by Mayasa of Spain.

The following results were achieved by the project:

- Draft regulation on hazardous wastes, National regulation on mercury added products, wastes and mercury wastes of import, export, cross-border transport, sale, use, storage and disposal was submitted to the government for consideration
- An interim mercury waste storage building was constructed and currently receiving mercury and hazardous wastes
- Initial site assessment and sampling were performed at the Boroo site; theoretical and field training on characterization were conducted; monitoring and pilot testing of three remediation technologies for mercury contaminated sites were demonstrated
- Training package of 8 brochures to raise awareness on mercury management was prepared and published in Mongolian
- A short video (in Mongolian) on the promotion of mercury waste management was broadcasted on three national TV channels to support a national wide campaign to collect mercury containing wastes
- The project presents an interesting case study and is one of the first successfully completed projects funded by the GEF in promoting mercury management at contaminated sites. The project can serve as an example for future technical cooperation project development.

1e: Advances in analytical methods for environmental mercury speciation

TO-049

INNOVATIONS IN MERCURY INDUSTRIAL AND ENVIRONMENTAL MEASUREMENTS

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Analysis of mercury often requires not only measurement of the total mercury content in the sample but also speciation studies of its inorganic (Hg0,Hg+1, Hg+2) and organic compounds (methylmercury). Many years experience of mercury measurements in industry (coal combustion, flue gases) and environmental samples (tissues, sediments, aerosoles, PM) performed by the authors has resulted in several modifications in instrumentation and methodology. The following innovationas will be presented with the examples of applications.

1. Portable system for continuous mercury speciation in flue gas and process gases.Effective reduction of mercury emission requires the application of speciation systems for emission control. In order to operate in flue gas the Nippon Instrument Corporation EMP-2 WLE-8 set was additionally equipped with the fly ash filter, steel probe, transfer line and the tee connector. The portable system was successfully tested in the laboratory and during the industrial tests in Poland and Czech Republic.

2. Automatic system for methylmercury determiniation. In order to facilitate the determination of methylmercury (MeHg) in biota samples with the headspace Tenax trap gas chromatography atomic fluorescence method, an automatic system was designed, constructed and tested. The system consists of Tekran 2500 detector, Gas Chromatograph (Hewlett Packard 5890), a pyrolysis unit, a Tenax trap with a heater, a flow unit, an Electronic Control Unit and a PC with Peak Simple software. A ten-stage mercury determination procedure was elaborated and optimized.
3. Portable Hg+2 ultrasonic calibrator for the control and calibration of mercury speciation systems. The calibrator generates a stable stream of HgCl2 (RSD=2.8% for Hg =28 ug/m3).
4. Innovative tests of non-carbon particulate sorbents in large scale demo installation in coal-fired power plant.
5. Innovations in methodology of performing data collection for the total particulate mercury (TPM) in PM10 and PM2.5 in many urban sites region of Southern Poland and Krakow agglomeration.

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TO-050

DETERMINATION OF HG SPECIES BY PHOTOCHEMICAL REDUCTION - AFS

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The most commonly employed technique for the determination of mercuryusing Atomic Fluorescence Spectrometry in a variety of matrices involves cold vapour generation. Usually, thisisachieved chemically by oxidising all organic mercury species to Hg2+, followed by a reduction to Hg0with SnCl2or NaBH4. However, this method usesa plethora ofchemicals which is costly andprone to error and instrumental issues due to the complex wet chemistry necessary.Another pathway is photochemical vapour generation (photo-CVG), whichhas been used inthe past inconjunction with CV-AFS as an alternative method of cold vapour generation. Previously, photo-CVG has been applied to total mercury measurements using formic acid. It has been shown that formic acid rapidly decomposes when subjectedto UV radiation, giving rise to species which easily reduce all mercuryspeciesto Hg0usingshort irradiation intervals. This methodpromises amuch simplerapproach, whichuses fewer and more environmentally friendly chemicals to give results which are comparableor even more sensitive thanthe cold vapour approach.However, the future of this technique lies in the ability to successfully apply this to mercury speciation. Thus, new LC-UV-CV techniques based on the method arebeing sought.One successful route used amethod whereby a 70/30 MeOH/H2O solution containing mercapto-ethanol as a mobile phase for reverse phase C18 separation,withon-line addition of formic acid: water samples spiked with Hg2+, MeHg+and EtHg+producedgood quality chromatogramsusing this approach. Inthis work, we apply this methodto a wide range of matrices such as wastewater, food, fish, and clinical samples.

TO-051

NEW TECHNOLOGIES FOR MEASUREMENT OF ATMOSPHERIC OXIDIZED MERCURY

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A growing body of evidence is showing that conventional, KCl denuder-based measurement systems for atmospheric oxidized mercury are biased low, and that the extent of bias depends on environmental conditions. To make matters worse, many of the oxidized mercury trends that have been observed may, at least in part, be the result of measurement bias. For example, very low ozone concentrations during Arctic mercury depletion events likely decrease oxidized mercury measurement bias, artificially enhancing the contrast between depleted plumes and background air. Similarly, dry, relatively pristine conditions in the upper atmosphere can be expected to decrease bias, clouding our picture of the vertical distribution of oxidized mercury. We must develop new measurement and validation techniques or we will never be able to gain a clear understanding of atmospheric oxidized mercury concentrations and cycling.

In response to this need, we are developing a suite of next-generation instrumentation for measurement and calibration of oxidized mercury. These include (1) an automated calibrator that can deliver stable concentrations of oxidized mercury compounds directly to the inlet of mercury instrumentation, verifying performance under ambient conditions; (2) A high-time resolution dual channel instrument to measure elemental and oxidized mercury, and (3) a GC/MS-based system to identify individual oxidized mercury compounds. We will discuss the development of and results obtained from these instruments. While they are not perfect, these instruments represent a vast improvement over conventional methods, especially because they incorporate routine verification of measurements in real-world conditions.

TO-052

POTENTIAL AND LIMITS OF MAGNETIC SOLID PHASE EXTRACTION USING CARBON NANOTUBES FOR MERCURY SPECIATION ANALYSIS

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The assessment of the health and environmental effects of mercury requires the precise and accurate determination of mercury species. Numerous techniques can be used for this purpose, but the low concentrations of mercury species usually found in environmental samples make necessary to include additional steps of preconcentration and/or cleaning in the sample preparation for mercury speciation analysis. Novel methodologies based on the use of new nanomaterials have been currently developed for trace metal analysis. A particularly promising combination is the application of magnetic nanoparticles coated with carbon nanotubes for solid phase extraction. It provides a fast and simple separation of analytes using an external magnet and avoids the time-consuming traditional on-column solid phase extraction procedures. However, this interesting approach did not have been applied up to now for the extraction of mercury species.

Therefore, in this work we have studied the potential of Fe3O4 magnetic nanoparticles coated with different types of carbon nanotubes (single, double and multi-walled) as sorbent material for the determination of mercury species. In all cases, mercury speciation analysis were carried out using gas chromatography coupled to atomic fluorescence detection after derivatization by ethylation. A careful optimization of the conditions affecting both sorption and desorption steps (i.e. type of carbon nanotube, amount of composite, time of sorption or desorption steps, desorbing medium) have been performed aiming to achieve an effective and selective preconcentration and subsequent analysis of monomethylmercury. Single-walled carbon nanotubes magnetic nanoparticles exhibited higher adsorption capacity compared to both double-walled and multi-walled carbon nanotubes. The reuse capability of these nanomaterials during several adsorption/desorption cycles has also been investigated. In addition, the potential interferences and/or interactions between mercury species in the sorption and desorption processes have been studied regarding different mercury species concentration ratios. The results demonstrated that the developed methodology enables not only the preconcentration of monomethylmercury but also the simultaneous clean-up of inorganic mercury.

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TO-053

IDENTIFICATION OF MERCURY SPECIES IN THE FLUE GAS OF COAL-FIRED POWER PLANTS

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Coal combustion is the largest anthropenic emission source of mercury in the world, but it is still unclear of the existing form of oxidized gaseous mercury in its flue gas. This study aims to explore the species of mercury in the flue gas of coal-fired power plants by HPLC-AFS. Gaseous mercury in the flue gas of a sedimentation furnace was sampled on nylon, PTFE and quartz membranes. Mercury adsorbed on various membranes was extracted by chromatographic grade acetonitrile and the sampling extrating solutions (ES1) was used to analyze the mercury species. Six mercury reference substance (Hg0, HgCl2, Hg2Cl2, HgO, HgS and HgSO4) were dissoved into acetonitrile solutions, which served as the reference substance solution, respectively. It was found that mercury capture efficiency of nylon, PTFE and quartz membranes were 72%, 35% and 28%, respectively. The HPLC-AFS result showed all of the three sampling extrating solutions (ES1) have three characteristic peaks at 211-218s (first), 257-268s (second) and 290-291s (third), and the three peak areas follow the order: first (1.1-18.2%) < second (19.5-29.5%) < third (52.4-78.0%). The characteristic peaks of six reference solutions appeared at 253-267s, belonging to the second mercury type. This result indicates that the six mercury references are not main existing form of mercury in flue gas, which is different from the traditional view that the HgCl2 is the main existing form of oxidized mercury in flue gas. The HPLC-MS/MS will be used to further identify the mercury species in flue gas in next stage.

TO-054

A NEW SIMPLIFIED METHOD FOR DETERMINATION OF MONOMETHYLMERCURY IN BIOLOGICAL SAMPLES BASED ON SEPARATION OF HG DITHIZONATES AND COLD VAPOUR ATOMIC ABSORPTION DETECTION

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Developments of new techniques for determination of monomethylmercury are primarily focused on high tech equipment, including mass spectrometry. However, methods based on mass spectrometry and other currently available instrumental techniques for speciation are based on principles that require clean laboratory conditions, expensive gases and a lot of experience. For most routine laboratories such conditions are unsuitable which results in the fact that speciation analysis are only done in expert laboratories. Moreover, recently adopted Minamata convention calls for simplified and easy-to-use methods that allow speciation of mercury world-wide.

Simple extraction method that can be used to measure monomethylmercury (MMHg) in biological samples has been developed. The method is based on the simultaneous extraction of Hg compounds into toluene as their dithizonates. Hg(II) and MMHg dithozonates are then separated on silica gel column and selectively collected into separate test tubes followed by digestion with mixture of acids (HNO3/HClO4 and H2SO4) and measured by CV AAS. The average repeatability and reproducibility of the method are 1.5% and 4.3%, respectively. Expanded relative standard uncertainty according to Nordtest is 12.8% using coverage factor k=2.

The method separates inorganic and organic mercury quantitatively in biological samples. Separation is very good also in samples where the percentage of MMHg is low. The results obtained were verified by the analysis of Certified Reference Materials and comparison of the results obtained by alternative methods based on ethylation and CV AFS detection.

Compared to other methods this method is simple and inexpensive from the point of view that the instrumentation which is used for total mercury measurements can be used to measure organomercury compounds. The detailed analytical methods as well as the results of MMHg in biological samples obtained using this method will be presented.

TO-055

DETERMINATION OF HG NANOPARTICLES IN PRODUCED WATER ASSOCIATED TO CRUDE OIL PRODUCTION BY SINGLE PARTICLE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (SP-ICP-MS)

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Mercury is one relevant element for many researcher due the potential impact to the enviromental as well as to humans. It recent years, many authors have determined the total concentrations and different species present in soils, atmosphere, water, biota mining and petroleum activities[1], particularly in petroleum business. Hg can be present in natural gas, crude oil and its products. The most dominant species are Hg^0 and Hg particulate, most likely associated to HgS[2-4]. Recently, some researchers reported that particulate HgS could be the most abundant species in stored petroleum hydrocarbons[5]. Additionally, when crude oil is extracted, the water used in the oil extraction and production consequently may contain Hg species, as Hg particulate. Researchers are now interested in determining if Hg nanoparticles are present in these waters. In an attempt to characterize these Hg nanoparticles, single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) has been employed. Sp-ICP-MS allows simultaneous determination of particle number, concentration and size, as well as measuring the dissolved metal concentration.

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TO-056

A NEW METHOD FOR DIRECT AND REAGENT-FREE BIOMONITORING OF MERCURY TRACES IN HUMAN URINE

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A novel analytical methodology for reagent-free sampling and extraction of mercury from human urine was developed and optimized. The method is based on selective separation of Hg from fresh urine sample onto active nanogold-coated silica material by highly efficient solid-phase extraction. The adsorbent for mercury extraction was prepared by chemical reduction of Au(III) to Au(0) in presence of silica. Subsequently, immobilization of formed gold nanoparticles is achieved by calcination. Characterization of this material by TEM, REM and TXRF confirmed the successful deposition of gold nanoparticles onto the silica, revealing an average particle diameter of 52 nm. Special in-house designed glass devices allow easy and quick extraction and separation of Hg from urine within only 10 minutes. After thermal desorption of Hg from the extractant, detection is performed by atomic fluorescence spectrometry (AFS). The feasibility and validity of the optimized, reagent-free approach was confirmed by recovery experiments in spiked real urine (recovery rate 96.13 5.34 %). Furthermore, mercury concentrations found in three (non-spiked) urine samples originating from occupationally exposed persons were compared to values obtained by application of the reference methods cold vapor - atomic absorption spectrometry (CVAAS) and CV-AFS. A very good agreement of the found values reveals the validity of the proposed approach. The limit of detection (LOD) was found to be as low as 0.004 ug Hg L-1 and a high reproducibility with a relative standard deviations 4.2 % (n=6) is given. Moreover, storage of the samples for up to one week at an ambient temperature of 30°C reveals no analyte losses or contamination. In addition, investigations revealed that calibration of one exemplary collector provides reliable quantification of all other collectors filled with extractant material coming from the same synthesis batch. Moreover, due to the re-usability of the material the proposed method is cost-efficient. In addition, it enables easy-to-handle on-site extraction of mercury traces from human urine ensuring at the same time reagent-free sample stabilization, providing quick and safe sampling, which can be performed by untrained persons.

TO-057

DEVELOPMENT OF A NOVEL PASSIVE SAMPLING STRATEGY FOR METHYLMERCURY IN SEDIMENTS AND SOILS

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Aquatic mercury can pose a significant risk to ecological and human health when it is converted to the more toxic and bioaccumulative methylmercury (MeHg) by anaerobic microorganisms near the sediment-water interface. Benthic animals exposed to MeHg in this zone represent an important link in the process of MeHg bioaccumulation in aquatic food webs. As such, quantitative measurements of the bioavailability of MeHg to benthos are critical for risk assessment of contaminated sites. To date, no passive sampling strategy has achieved wide acceptance for generating such measurements. The diffusive gradient in a thin film (DGT) device, which operates in a kinetic accumulation mode, faces questions about the potential for oversampling, as well as the identity of the MeHg species it samples and their relevance to bioavailability. We are working to develop a novel passive sampling technology to emulate the steady-state (pseudo-equilibrium) mode of MeHg bioaccumulation by benthos. A target range of sampler partitioning was set at log K between 3.0 and 4.5 in consideration of analytical detection limits, the logistics of sampler deployment in the field, and typical sediment-water partitioning constants. A variety of custom polymers with either reduced sulfur chemical functionality or embedded activated carbon (AC) particles was prepared and evaluated in a series of increasingly environmentally realistic experiments. In mildly saline water isotherms, many of the materials showed strong, log-linear partitioning of MeHgCl across a relevant range of concentrations. Partitioning of MeHg complexed with dissolved organic matter was decreased but still in or near our target range (log K = 2.83 to 3.31). In slurries of contaminated soil, polymer-predicted water concentrations (Cw) were within factors of one to five of directly measured water samples. In beaker soil microcosms, accumulation of MeHg by our AC-based polymer successfully reflected temporal variations in Cw as well as reductions due to amendment of soil with AC. Polymer-derived and directly measured Cw agreed equally well at 8, 14, 21, and 28 d of exposure. Across experiments, partitioning by this polymer was notably consistent in the saline water, slurry, and unamended beaker soil (log K = 3.41 to 3.78). An experiment currently being planned will attempt to correlate MeHg accumulation by polymers and by the amphipod L. plumulosus exposed side-by-side in sediment microcosms. The polymer data will be used as input for a bioaccumulation model to evaluate the technologys predictive capability.

2a-1: Sources and cycling of mercury in coastal ecosystems

TO-059

RIVERINE INPUTS TO NORWEGIAN FJORDS: EFFECTS ON LOWER FOOD WEB STRUCTURE AND MERCURY BIOACCUMULATION

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Climate change is expected to drive increases in terrestrial organic matter (OM) export to northern aquatic systems, including Norwegian coastal waters. The coastal environment is also influenced by inputs of contaminants that can pose human and ecosystem health risks. There is an increasing need to gain an understanding of how changes in terrestrial inputs to coastal waters can drive changes in ecology and contaminant dynamics in order to predict future impacts and develop effective management approaches.

Here, we characterize physicochemical conditions, lower food web ecology and mercury (Hg) bioaccumulation along two Norwegian river-fjord gradients, one in southern Norway (Storelva-Sandnesfjord) and one in subarctic Norway (Mlselv-Mlselvfjord). Briefly, seasonal water and zooplankton samples were collected along both river-fjord gradients in 2015-2016, for characterisation of physicochemical conditions, lower food web structure (using dietary markers) and Hg trophodynamics.

Physicochemical conditions along the study transects were primarily driven by conservative mixing of the fresh and marine water masses, and the rivers were an important source of silicate, Hg, and terrestrial OM to the coastal waters. Based on dietary marker analysis, near-shore zooplankton utilized terrestrial inputs as a food source, with decreasing importance of terrestrial energy sources with increasing distance from the river outflows. Hg concentrations in zooplankton were typically highest for inner fjord sites and decreased along the study transects. Estimated Hg bioaccumulation factors for zooplankton also tended to decrease along the study transects, suggesting that the elevated Hg concentrations in zooplankton from the inner fjord stations were attributable not only to the elevated Hg concentrations in inner fjord water, but also to more efficient bioaccumulation of Hg at the sites with higher freshwater influence.

These results suggest that riverine inputs to Norwegian fjords can have strong impacts on physicochemical conditions, ecology and Hg dynamics, highlighting a need for more detailed understanding of the seasonality and spatial extent of this influence, as well as the implications of future climate change driven increases in riverine inputs to Norwegian coastal waters.

TO-060

TERRESTRIAL ORGANIC MATTER DISCHARGES ENHANCE MERCURY REDUCTION AND EMISSION FROM ESTUARINE SEDIMENTS

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Legacy Hg burial in aquatic sediments represents one of the largest reservoirs for anthropogenic Hg, which can potentially be reemitted back to the atmosphere. However, the rates and controlling factors for emission of Hg from sediments, especially Hg-contaminated sediments, remain unclear. We determined emission rates of gaseous elemental mercury (Hg0) from contaminated fiber-rich water-sediment microcosms under a wide range of redox conditions using geochemical relevant isotopic-enriched divalent Hg (HgII) tracers: 201Hg(NO3)2, 202Hg-NOM (HgII bound to natural organic matter) and β-198HgS(s) (microcrystalline metacinnabar). Up to one order of magnitude higher Hg0 emission rates were observed in anaerobic surface sediments (0-2cm) dominated by terrestrial organic matter, as compared to organic fiber dominated deeper sediment (0-10cm). β-198HgS(s) showed 15 times lower Hg0 emission rate than the other two tracers due to its low solubility. We suggest that the reductive power of aromatic functional groups (e.g., quinone and semiquinone) of terrestrial organic matter drives rates of HgII reduction and emission. We further conducted separate incubation experiments where the chemically reduced quinone compound AQDS or terrestrial organic matter (Suwanee River NOM) were added to the water-sediment microcosms. Elevated Hg0 emission from the HgII isotope tracers and ambient Hg were observed. Our results highlight that terrestrial organic matter discharged into the estuarine sediments act as electron shuttles, enhancing legacy Hg reduction and subsequent re-emission to the atmosphere. Further results on HgII reduction and emission in the presence of marine autochthonous organic matter (i.e. algae and cyanobacteria derived organic matter) will also be presented and discussed.

TO-061

ORGANIC MATTER DRIVES HIGH INTERANNUAL VARIABILITY IN NET METHYLMERCURY PRODUCTION IN A SUBARCTIC COASTAL SEA

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Methylmercury (MeHg) levels in aquatic ecosystems are strongly driven by organic matter (OM), however, we have a poor understanding of how spatial and interannual variability in the composition and concentration of OM within ecosystems control MeHg levels. To address this we determined MeHg concentrations and methylation/demethylation rate constants in water samples during late summer/early fall (2014-2016) in a subarctic coastal sea (Northern Baltic Sea). We furthermore compiled 11 years of data (2006-2016) for dissolved organic carbon (DOC) and humic content. We find that the average MeHg concentrations in offshore waters have large interannual variability (2014: 80±25 fM; 2015: 11±11 fM; 2016: 21±9 fM). We create a statistical multiple linear regression model using MeHg concentration, DOC and humic content. We show that 60% of the spatial and interannual variability in MeHg concentration in the Northern Baltic Sea can be explained by changes in DOC and humic content. The seasonal variable DOC reservoir (mostly marine DOC in offshore waters) caused an increase in MeHg concentrations. This is consistent with the prevailing hypothesis that MeHg is produced in situ in the water column during OM remineralization. Contrary to this, an increase in humic content lowered the MeHg concentration, indicating less bioavailability of HgII in the presence of humic substances. We apply the model to examine the extent of interannual variability driven by DOC composition and concentration for summer/fall MeHg concentrations between 2006 and 2016 and find a range from below detection limit (2007-2008: 13 fM) to 150 fM (2012) in offshore waters. We will present results from the study and discuss implications for food webs. We will furthermore reflect on how anticipated changes in river exports of nutrient and OM due to climate change will influence MeHg concentrations in similar systems.

TO-062

INFLUENCE OF DISSOLVED ORGANIC CARBON ON MONOMETHYLMERCURY UPTAKE IN TEMPERATE AND POLAR MARINE DIATOMS

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Phytoplankton are the primary route of entry for monomethylmercury (CH3Hg) into the food web of the upper ocean (<1000 m) leading to elevated concentrations in pelagic migratory fish, a significant route of human exposure. Laboratory experiments were conducted in which the accumulation rates of intracellular CH3Hg were measured in two species of temperate marine diatoms, Thalassiosira weissflogii (Tw) and Thalassiosira psuedonana (Tp), and one species of polar diatom, Chaetoceros brevis (Cb), along with initial dissolved organic carbon (DOC) in synthetic ocean water (SOW), and DOC excreted by phytoplankton cells into SOW following CH3Hg exposures. At typical initial background DOC concentrations (~2 mg/L), short-term (<1 hr) uptake rate constants of CH3Hg normalized to cell biomass and CH3Hg concentrations were higher in Tp (3.80 L g-1 h-1) than in either Tw (0.36 L g-1 h-1) or Cb (0.16 L g-1 h-1). However, higher rate constants were observed in Tw at lower (<1 mg/L) DOC concentrations (1.02, 2.96 L g-1 h-1). A nonlinear relationship between CH3Hg uptake rates and initial DOC concentration was observed across multiple experiments

for Tp (r2=0.99) and Tw (r2=0.87). DOC concentrations in incubations of Tw with CH3Hg increased over time to values that were 3 to 40 times higher than those in control experiments without CH3Hg suggesting that exposure to CH3Hg stimulated DOC production by this diatom. The observed decrease in CH3Hg uptake rates from 1 to 24 h of exposure indicates that DOC excreted by diatoms in response to CH3Hg exposure may influence CH3Hg speciation and bioavailability. Small differences in seawater DOC concentrations in the oligotrophic open ocean and larger changes in DOC in productive coastal waters may influence the speciation of CH3Hg therefore affecting its enrichment at the base of the marine food web and subsequent human exposure from higher trophic level fish.

TO-063

METHYLMERCURY CYCLING IN THE YELLOW SEA AND BOHAI SEA, CHINA: SOURCES/SINKS AND CONTROLLING FACTORS

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The Yellow Sea (YS) and Bohai Sea (BS), economically important regions of the western Pacific Ocean, have been facing a variety of environmental problems, including mercury (Hg) pollution. Although methylmercury (MeHg) has been recognized as the most toxic Hg species in the environment, there is still a lack of knowledge on its cycling in the BS and YS, limiting a sound understanding of Hg cycling in both regions. To address these needs, we investigated the distribution and methylation/demethylation of Hg in both regions during two marine science cruises. A decreasing trend from inshore to offshore was observed for both total Hg (THg) and MeHg, suggesting the importance of terrestrial discharge. Methylation in the sediment and photodemethylation in the water were identified as the two most important processes controlling MeHg levels, while SO42-, THg, and dissolved organic matter were found to be the most influential environmental factors. By quantifying the in situ production/degradation, along with river input and exchange with nearby seas, sediment was found to be the most important source of MeHg; meanwhile, the water serves as the largest sink in both regions. In comparison with other marine systems, a relatively low ecosystem conversion efficiency of inorganic Hg to MeHg, i.e., low MeHg/THg ratios in the water, was observed in the BS and YS. This may result from the low efficiency of transporting THg from water to the sediment, slow methylation in the sediment, and quick photodegradation in the water. The low conversion efficiency of inorganic Hg to MeHg may be one of the convincible reasons for the low Hg levels detected in the YS and BS organisms, in comparison to the high THg concentrations in the water.

TO-064

MERCURY AND METHYLMERCURY IN CHESAPEAKE BAY WATERSHED: LOOKING FOR CHANGE IN A CHANGING WORLD

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Measures to lower Hg emissions in the US have been ongoing over the past 2 decades. Observing and quantifying the impact of these reductions in the environment is difficult given the changing mixture of local and global sources and the complex cycling and recycling of mercury in the ecosystem. In this presentation we summarize Hg monitoring and research in the Chesapeake Bay watershed, with the aim of detecting changes in fluxes or risk. Studies include long-term wet-deposition measurements, including MDN network measurements from the 3 Maryland stations (since 2005); small-watersheds fluxes (since 2008), and entry into biota (Young of the Year fish (YOY), since 2008). These studies have been specifically designed to identify changes to Hg cycling in the Chesapeake Bay watershed.

Year to year variability in wet deposition is substantial. Importantly however, Hg wet deposition loadings to the Mid-Atlantic appear not to have declined over the last decade or so in concert with regional estimated emission reductions. Although there have been some decreases in the average Hg concentration in rain and loadings in urban areas.

Year to year variability in Hg export from small streams is substantial (varying on the order of 5x for both T-Hg and MeHg) and largely dependent on hydrologic variables. Needless to say and we cannot detect a temporal pattern to date.

We have almost a decade of young of the year fish monitoring in the Chesapeake Bay and in watershed reservoirs. Differences in concentrations of mercury in the YOY fish populations among the 13 sites cover an order of magnitude. Year to year variability among the sites also varies, suggesting watershed characteristics and/or reservoir management impact the cycling of mercury to differing degrees among the sites, but no temporal trend in the data has been observed to date.

In this study, we have observed that changes in land-use, population and climate, even over the short duration studied, adds complexity to the watershed flux and biota metrics. Our understanding of the Hg and MeHg budget to the Chesapeake Bay has also evolved. High concentrations of Hg and MeHg in export water of small streams of the coastal plain, combined with their large number, make them a source that rivals the large rivers; which have high flow but low concentrations of Hg and MeHg.

TO-065

WATER COLUMN METHYLMERCURY, ORGANIC MATTER AND SEDIMENT-WATER FLUX ACROSS A LATITUDINAL GRADIENT ON THE US EAST COAST

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The potential effects of climate change in coastal ecosystems include increased rainfall with subsequent runoff from watersheds and increased carbon flux to sediments. These factors should increase the watershed delivery of mercury (Hg) to the estuarine water column and increase sediment anoxia, Hg content and Hg methylation. To examine these potential outcomes, we evaluated methylmercury (MeHg) sources at sites with high and low organic matter sediment in 6 small salt water creeks and wetland areas in Maryland (MD), Connecticut (CT) and Maine (ME; temperature range of 20 to 29 degC; sampled in 2013). Average dissolved MeHg (0.05 to 6.3 pM; 3 to 35% MeHg), suspended particle MeHg (1.1 to 84 pmol/g; 1 to 17% MeHg) and dissolved organic carbon (DOC; 0.1 to 3.3 mM) increased with latitude, and were highest at CT salt marsh and ME sites. Average sediment MeHg (0.04 to 3.5 pmol/g) and organic content (loss-on-ignition; 0.7 to 25%) also increased with latitude. Dissolved MeHg and total mercury (HgT) were correlated among sites along the latitudinal gradient, and this was also the case for suspended particle concentrations. However, average suspended particle MeHg concentrations were higher (factor of 3 to 550) than sediment MeHg levels at each site, particularly at sites in ME and CT, suggesting watershed sources of suspended particle MeHg to the creeks sampled. Similarly, dissolved MeHg concentrations at sites in ME were a factor of 1.5 to 30 higher than pore water MeHg levels. Sediment flux cores were used to measure sediment-water MeHg flux, and site average fluxes ranged from 10 to 360 pmol/sq m/d in MD and CT, which is similar to the range found for other US estuaries. However, large negative fluxes of -280 to -500 at the ME sites indicate that water column MeHg was partitioning into the sediment, and that the creek watersheds were likely supplying the elevated dissolved MeHg. Dissolved MeHg was strongly correlated with DOC across all sites, and both dissolved MeHg and HgT were highest at sites in ME where DOC was highest. Our research indicates that watershed sources of MeHg are important to Hg loading in shallow estuaries and that delivery and concentrations of MeHg in the water column appear to be regulated by organic matter.

TO-066

SEDIMENT WATER FLUX OF MERCURY SPECIES ON THE CONTINENTAL MARGIN BETWEEN SOUTHERN CALIFORNIA AND CENTRAL OREGON

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Monomethylmercury (MMHg) production by anaerobic bacteria in sediments is considered to be a dominate source of MMHg to sediments and overlying surface water in the coastal environment. In this study, we measured total mercury (Hgt) and MMHg sediment and pore water concentrations and calculated sediment water exchange fluxes in samples collected on the coastal shelf in the California Current System. Sediment cores and overlying water were collected from 20 stations using a slow-entry multi-corer deployed during 4 oceanographic cruises over two years. The upper few centimeters of undisturbed cores were sectioned at the following depth increments: 0.5, 1, 1.5, 2, 3, 4, 5 cm. Pore waters were extracted via centrifugation and the MMHg gradients were used to calculate fluxes into the overlying water column based upon molecular diffusion alone. Sediment concentrations for Hgt and MMHg ranged from 50 to 2338 pmoles g-1 and 0.1 to 9 pmoles g-1 respectively. Pore water and overlying water MMHg concentrations ranged from 0.1 to 2.2 pM and 0.03 to 0.3 pM respectively. Diffusional MMHg sediment water exchange flux ranged from 0.1 to 1.7 pmoles m-2 d-1. While the gradients in MMHg showed significant and widespread flux that would indicate an input into the waters of the shelf these fluxes were very small compared to those calculated elsewhere and insufficient to sustain elevated concentrations at the sediment boundary layer, or at the depth of the shelf in general. Measurements made on the northwestern Atlantic shelf are in general an order of magnitude greater than those observed here. We suggest that the narrow eastern shelf of the California Current with little allochthonous inputs contrasts sharply with the broad shelf of the Eastern Seaboard with significant organic carbon, riverine and anthropogenic inputs. In general, the narrow shelf of the California Current seems to reflect the pelagic processes of the off shore regions for this element where water column production predominates the formation of the methylated forms.

2b-2: Sources and cycling of mercury in freshwater ecosystems: Dedicated to the memory of George Aiken

TO-067

EFFECTS OF BELOWGROUND WARMING ON PEAT POREWATER TOTAL MERCURY AND METHYLMERCURY CONCENTRATIONS: EARLY RESULTS FROM SPRUCE

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The Spruce and Peatlands Under Climatic and Environmental Change (SPRUCE) Experiment is pushing the envelope assessing the effects of whole ecosystem warming on numerous ecosystem processes. As part of the SPRUCE framework we sampled peat porewaters at 0, 30, 50 and 100 cm for totalmercury (THg)and methylmercury (MeHg) across five temperature treatments (0oC or ambient, 2.25oC, 4.5oC, 6.75oC, and 9oC) during the 2016 unfrozen period beginning in June and ending in November. Both aboveground and belowground warming is a differential compared to outside the SPRUCE chambers and belowground warming extends to >2 m. Porewater THg concentrations at 0 cm depth were significantly higher in the 6.75oC and 9oC treatments than at the 0oC, 2.25oC and the 4.5oC treatments which were similar. At 30 cm there was an opposite effect where the 9oC treatment had lower THg concentrations than at lower temperature treatments. Below 50 cm there were few temperature treatment effects on THg. Porewater MeHg concentrations were highly variable at 0 cm depth with no significant differences among temperature treatments. At 30 cm depth, the 0oC treatment was significantly lower than the 4.5oC, 6.75oC and nearly different than the 9oC treatment. At 50 cm depth all temperature treatments had significantly lower concentrations than the 9oC treatment. We had few MeHg samples above detection at 100 cm depth. Our initial data indicates that elevated soil temperatures increase peat pore water MeHg concentrations in the 30-50 cm depth zone, while also increasing THg in surface waters, but we unexpectedly found decreases in THg at the highest temperature treatment in the 30 cm zone, with few other differences below 30 cm. We will discuss possible mechanisms that lead to these results and larger implications for Hg cycling with climate change.

TO-068

MERCURY AND METHYLMERCURY IN TRIBUTARY INPUTS TO KLUANE LAKE, YUKON TERRITORY, CANADA

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Kluane Lake is located in the southwest of the Yukon Territory, Canada, and is part of the traditional territory of the Ln Mn Ku Dn, the Kluane Lake People. The community depends on Kluane Lake as an important source of subsistence food fishes, and the lake is well known for supporting healthy populations of Lake Trout and Lake Whitefish. Although situated in a relatively remote and pristine region, community interest in contaminant levels in food fishes supported intensive research on mercury (Hg) in the biotic and abiotic compartments in Kluane Lake, and instigated a pilot-scale investigation of Hg, methylmercury (MeHg) other metals and related ancillary measurements in the waters and sediments of its tributary inputs. We found that total Hg concentrations ([THg]) varied considerably among tributaries (<0.05 to 1.1 ng/L for filtered, and from 0.1 to 25 ng/L unfiltered), with elevated unfiltered [THg] largely reflecting a significant suspended sediment load in some glacier-fed streams. Methyl mercury concentrations ([MeHg]) were below detection (0.006 ng/L) for many streams, but two of the larger tributaries to the lake (Burwash Creek and Gladstone River) had measureable MeHg concentrations (0.010 0.040 ng/L). However, the volumetrically largest inflow to Kluane Lake, the Slims River, had dissolved [THg] and [MeHg] below detection. An examination of other water chemistry variables related to [Hg] found important relationships among [Hg], [MeHg] and the quantity and quality of dissolved organic carbon (DOC) in tributary waters. Dissolved [MeHg] was positively related to total DOC. There was no relationship between [THg] and total DOC, but [THg] was inversely related to fluorescence measures of organic matter freshness, and positively related to measures of organic matter humification, suggesting that dissolved [THg] is being derived from well-humified sources of organic matter. Currently, Kluane Lake has extremely low dissolved Hg concentrations because the largest, glacially-dominated tributary input (Slims River) has exceptionally low Hg and DOC. As the importance of glacier melt-derived inputs decrease, the relative importance of other higher Hg and DOC tributaries will increase. Although all waters in this catchment are dilute, climate-change driven shifts in runoff could ultimately drive a shift in lake water chemistry and Hg availability in the future.

TO-069

EFFECT OF LOW-MOLECULAR-WEIGHT ORGANIC ACIDS ON MERCURY TRANSFORMATION IN SOIL IN WATER-LEVEL FLUCTUATION ZONE OF THREE GORGES RESERVOIR, CHINA

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According to the planning and design, the water level of Three Gorges Reservoir fluctuates between 145 and 175 m, which forms a water-level fluctuation zone (WLFZ) occupying areas of more than 400 km2. Soil low-molecular-weight organic acids (LMWOAs), mainly originated from the decomposing organic matter, root exudates and microbial

metabolites, are important ligands involved in complexation reactions of heavy metals and hence, their bioavailability. The WLFZ became periodically alternated wetting and drying resulting in the vegetation suffered inundation (decomposition) and growth, which may influence the Hg bioavailability in soil and bioaccumulation in aquatic food chains as the produced LMWOAs from plants. In Aril of 2016 to September, seven common LMWOAs including Citric acid (CA), Oxalic acid (OA), Tartaric acid (TA), Acetic acid (AA), Propanedioic acid (PA), Succinic acid (SA), Malic acid (MA) from root exudates, rhizosphere soil and bulk soil in WLFZ were sampled and analyzed. Then, LMWOAs (CA, TA and OA) were chosen to investigate their effect on the Hg behavior in WLFZ soil. Results were followed as, 1. TA and OA occupied for a higher percentage in root exudates, rhizosphere soil and bulk soil, but PA and CA were just different. Due to the biodegradation and clay adsorption, a lower LMWOAs concentration (M) in bulk soil was found compared to that in rhizosphere soil (mM). Statistical analysis showed a significant difference among various LMWOAs in root exudates, rhizosphere and bulk soil. 2. The presence of OA, TA, and CA promoted Hg desorption from soil to solution, and the increasing bio-available Hg speciation was found as the increasing LMWOAs concentration, which may be due to the complexation of carboxyl groups and ion exchange reactions at mineral surface. Compared to the control groups, LMWOAs increased the ratio of methylmercury to total Hg of 2.72%,1.76%, 2.02% for CA, OA and TA in anaerobic condition, respectively, which were higher than that in aerobic condition, indicating a stimulated Hg methylation was anaerobic microbes other than aerobic microbes caused by LMWOAs. Furthermore, the coexistence of various LMWOAs could enhance the activation effect to soil Hg of WLFZ.

TO-070

SEASONALITY OF MEHG INPUT, OUTPUT, FORMATION AND DEGRADATION IN A HUMIC BOREAL LAKE IN RELATION TO THE CHEMICAL SPECIATION OF HG, FE AND S

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Lake Ängessjön is a shallow (2.5 m maximum depth) humic boreal lake of 0.7 km2 in northern Sweden having concentrations of Hg in fish exceeding the limit set by health authorities for regular consumption of 0.5 mg kg-1 fw if standardized to1-kg pike. The total catchment area of 3.9 km2 is composed of 56% forest soils, 15% peatland soils, 10% agricultural soils and 18% lake water. Terrestrial runoff contributes about 85 % of Hg and >95% of MeHg external sources to the lake. Annual input-output budgets for 2007 and 2009 proved the lake to be a sink for Hg (16-30 % of input), MeHg (11-33% of input) and organic carbon (7-26% of input). The lake sediments provided seasonaly variable internal sources of MeHg (Hg methylation) and sinks of MeHg (demethylation). Rates of both processes were highest in the top 0-3 cm sediment and peaked during mid-summer in concurrance with maximum water temperatures and sedimentation rates of autochthonous (algal) organic matter. MeHg demethylation rates in the sediment showed an additional peak during winter. Photolysis of MeHg in the water column reduced its concentration in the bottom water drastically during summer, depleting (by diffusion) MeHg also in the top 0-3 cm sediment. Deeper sediment (3-10 and 10-20 cm) showed a clear seasonal variation in MeHg concentrations with a minimum during summer and a maximum during winter. The solubility and chemical speciation of Hg could be explained by reactions with reduced sulfur species, varying with season and depth in sediments. Because of the limited water depth, the lake does not stratify during summer and sulfide is not detected in the bottom water any time of year. In the top sediment, FeS and S0 were important components providing conditions for polysulfide formation and keeping the dissolved sulfide concentration stable between 0.5 and 2.0 µM in apparent equilibrium with the amorphous mineral mackinawite (FeSm). In deeper sediment, crystalline FeS2 (pyrite) was the dominant form (>60%) of sulfur. The concentration of organic thiol functional groups (RSH) associated with NOM was determined by use of Hg EXAFS spectroscopy. Thiols represented 7% of total S in the sediment. Thermodynamic modelling, using the latest updated constants for the formation of metacinnabar (β-HgS) and the complexation of Hg to RSH groups could reasonably well explain porewater concentrations of Hg by depth and season. We conclude that the activity of methylating anaerobic bacteria, driven by increasing temperatures and high availability of electron donors in concert with increased concentrations of dissolved Hg-sulfide and -polysulfide complexes, increased rates of MeHg methylation in boreal lake sediments during summer. Also MeHg import from terrestrial sources was significant. Yet, MeHg was net-degraded in the lake because of the very efficient photolysis of MeHg in the water column.

TO-071

DISSOLVED ORGANIC MATTER AND NUTRIENT CONTROLS ON AQUEOUS MERCURY SPECIATION IN ALASKAN WETLANDS

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In northern wetlands, sulfate availability is well-recognized as an important environmental variable influencing the conversion of divalent mercury (Hg(II)) to bioavailable methylmercury. However, no efforts to date provide a complete account of mercury behavior in northern wetlands by also investigating the controls on (1) total mercury abundance and (2) the dark reduction of Hg(II) to dissolved gaseous mercury (Hg(0)), a transformation proposed to limit mercury retention and bioavailability in ecosystems. A complete understanding of the factors controlling the distribution of mercury between relevant aqueous species (Hg(II), methylmercury, Hg(0)) in northern wetlands is needed to predict mercury behavior, especially considering the changes in wetland hydrologic connectivity and nutrient status expected as a result of continued warming of northern environments.

This study explores the biogeochemical controls on mercury abundance, methylation, and dark reduction in eight Alaskan wetlands that differ in nutrient status. Wetlands, selected to span a continuum from ombrotrophic bogs to minerotrophic fens, were sampled in interior and southcentral Alaska in the summers of 2015 and 2016. Concentrations of pore water constituents (dissolved organic carbon (DOC), inorganic anions, major cations, simple organic acids, sulfide) and compositional differences in dissolved organic matter (DOM) aided the interpretation of the environmental controls on mercury behavior in wetlands. Associations of Hg(II) with dissolved organic matter (DOM) were central to mercury abundance in the wetlands, as supported by site-specific correlations between pore water DOC and total mercury concentrations. Methylmercury formation in bog pore waters was minimal due to sulfate limitation, whereas methylmercury formation in fens was explained by the availability of inorganic mercury and sulfate. Good agreement was observed between the relative abundance of methylmercury in wetlands and estimated rates of Hg(II) methylation, the latter measured by stable mercury isotope injections in peat cores. Results identify sulfate-rich fens as critical locations for methylmercury formation. Across all wetlands, the relative abundance of Hg(0) was inversely related to DOC concentration, which suggests that mercury-DOM interactions limit dark Hg(0) formation in pore waters. Relationships between the absolute and relative concentrations of methylmercury and Hg(0) were not observed. Insights on the role of pore water constituents on mercury abundance and speciation in Alaskan wetlands are discussed in context of future hydrologic conditions expected in northern latitudes in response to a warming climate.

TO-072

THE ROLE OF DOM IN CATCHMENT AND LAKE MERCURY CYCLING IN A BOREAL LAKE CATCHMENT

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In the ecological research lake catchment Langtjern in southern Norway, monitoring programmes collect data on streamwater and lake chemistry, hydrology and climate. Here, we present 10 years of data of mercury species (Hg, MeHg) in inlets and outlet, 5 years of lake depth profiles on Hg and MeHg, in addition to dissolved organic matter (DOM) size fractionation and degradability. The data are collected to infer catchment and lake processes on mercury and DOM cycling and foodweb exposure to Hg.

We observe significant declines in streamwater concentrations of MeHg, MeHg to TOC ratio, and the MeHg to HgT ratio (a proxy for methylation potential). No temporal change is found in concentrations of Hg, TOC, and the Hg to TOC ratio. In the inlets, summer concentrations of MeHg are significantly ($p<0.01$) higher than in other seasons, while seasonal variation of MeHg in the outlet is minimal. Seasonal variation in HgT is stronger than for MeHg and appears to be associated with variation in TOC. In the outlet, the Hg to TOC ratio is significantly ($p<0.0001$) higher than in the inlets, which suggests that DOM is retained and removed in the lake while Hg is redistributed to remaining DOM compounds. Significant (5-20% of annual inputs) removal and retention of DOM is confirmed by an input-output budget of DOC for the lake. The Hg to TOC ratio in the streams is lower than in the lake, while the MeHg to HgT ratio at 1m depth is lower than at higher depth, possible reflecting losses of MeHg from photo-oxidation.

Size fractionation of DOM (tangential ultrafiltration) and studies of biodegradability of size fractions (measured as oxygen consumption) show evidence of significant changes between inlet and outlet in size fraction, biodegradability of fractionated DOM and Hg associated with the different size fractions. The smallest size fraction (<100 kDa) contains a larger proportion of the DOC in the outlet compared with the inlet, and is most labile in the outlet (expressed in oxygen consumption per g DOC).

Additionally, the Hg to DOC ratio for all size fractions is largest in the outlet. This may imply that the base of the aquatic foodweb, especially for organisms relying on bacteria as energy source, in the outlet is more exposed to Hg than in the inlets. Bacterial consumption of easily degradable, Hg-contaminated DOM is thought to be an important pathway for Hg into the aquatic foodweb.

TO-073

DISSOLVED ORGANIC MATTER CONTROLS MERCURY PHOTOREACTIONS IN WATER

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Methylmercury (MeHg) contamination through bioaccumulation and biomagnification is an issue in many remote ecosystems far from direct pollution sources. Quantifying why and how some ecosystems are more sensitive to contamination following atmospheric mercury deposition is key to mercury fate modeling. While we know bacterial pathways dominate the mechanism of mercury methylation, the demethylation of MeHg is less understood. Photodemethylation is thought to be one of the main processes through which MeHg can be converted into a less biologically toxic form of mercury. Previous studies highlight the importance of photodemethylation to mercury budgets, yet few have examined the magnitude and variability of photodemethylation rates as a function of associated dissolved organic matter (DOM). A temporal comparison study between summer and fall was conducted using lake water collected from 6 lakes in Kejimkujik National Park, Nova Scotia, Canada. Sample lakes were chosen based on a known range of DOM concentration. Lake waters were filtered to 0.45 m and placed in closed polytetrafluoroethylene (PTFE) bottles with >50% headspace, spiked with 3 ng/L MeHgOH, and exposed to 0, 1, 2, 3, 5, and 7 days of natural solar radiation in each experimental season. Lakes with higher DOM concentrations had significantly lower rates of photodemethylation than lakes with lower DOM concentration ($p<0.001$). Additionally, there were negative linear relationships between rates of MeHg photodemethylation and rates of DOM photomineralization (R2s=0.58-0.72) and DOM photobleaching (R2s=0.83-0.90). This key finding suggests that competition for photons by DOM may reduce the potential for MeHg photodemethylation in high carbon waters and that this relationship persists across seasons.

TO-074

PROBING THE DOM-MEDIATED PHOTODEGRADATION OF METHYLMERCURY BY USING ORGANIC LIGANDS WITH DIFFERENT MOLECULAR STRUCTURE AS DOM MODEL

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Photodegradation is the main depletion pathway of methylmercury (MeHg) in aquatic environments. The formation of MeHg-dissolved organic matter (DOM) complexes is a key step in MeHg photodegradation. However, the major functional groups in DOM mediated MeHg photodegradation have yet been clear. In this work, we systematically investigated the effects of DOM molecular structures on MeHg photodegradation by using a variety of organic ligands with different functional groups (e.g., thiosalicylic acid, thiophenol, and thioaniline). The results showed that thiol and phenyl groups may be the major functional groups in DOM dominate MeHg photodegradation, and the photodegradation rates also depends on the type (carboxyl, hydroxyl, amino group) and position (ortho-, meta-, para-) of other substituents. In addition, the addition of non-photochemically-active thiol ligands (e.g., mercaptoethanol and dithiothreitol) and high concentration Cl- could significantly inhibit the o-thiosalicylic acid-induced MeHg photodegradation, indicating that complexation of MeHg with theses ligands are necessary for MeHg photodegradation. Sparging with O2 has negligible effect on MeHg photodegradation, while sparging with N2 significantly enhances MeHg photodegradation. This finding suggests that MeHg photodegradation may be a reductive process, which was further supported by identifying the degradation products of MeHg.

2g-1: Legacy site assessment and management

TO-075

THE ROLE OF DETRITUS IN DEFINING MERCURY UPTAKE IN AN URBAN ESTUARY

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The Berrys Creek Study Area (BCSA) Superfund site is a 4.2 km2 tidal tributary to the Hackensack River in Bergen County, New Jersey. The site includes 4.2 km of waterways, surrounded by 3.1 km2 of intertidal marshes dominated by Phragmites australis. Mercury is among the chemicals of potential concern (COPCs) at the site. We designed a phased, conceptual site model (CSM)-oriented investigation that integrated information on the physical, chemical, and biological conditions of the site and the region to assess site-specific uptake.

Multiple lines of evidence collected during the remedial investigation indicate that mercury uptake in the BCSA is mediated via a detrital-based food web. Empirical relationships developed for mercury in shallow sediments and surface water across a range of spatial scales indicate the importance of sediment as the source of mercury for biological uptake. Mercury residues in detritus at the surface of the marshes and in the topmost layer of waterway surface sediments are low relative to deeper sediments, thereby limiting availability of mercury for biouptake; the flat trophic structure of this urban, low-salinity estuary limits biomagnification. In both marsh and waterway sediments, the organic carbon levels, sulfides, and other physical/ chemical characteristics also limit mercury bioavailability.

High resolution, optically-based monitoring and other measurements demonstrate that marsh-derived detritus settles to the waterway sediment bed during slack tides to form a thin, benthic layer of low-density organic material on which mercury and methyl mercury can be sorbed. Resuspension of these materials during high tidal velocities and storm flows is a primary mechanism for mercury and methyl mercury transport to surface water. Empirical relationships developed for mercury in shallow sediments and surface water across a range of spatial scales indicate the importance of sediment as the source of mercury for biological uptake.

TO-076

UNDERSTANDING THE REDISTRIBUTION AND BIOGEOCHEMICAL CYCLING OF MERCURY IN A CONTAMINATED FLOODPLAIN

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The Androscoggin River near Berlin, NH flows past a Superfund site that, prior to 1962, was a chlor-alkali facility. Leakage of elemental Hg from the site directly into the river was reported during site characterization in the late 1990s and had likely been occurring for decades. Despite remediation efforts that concluded in 1999, as recently as 2010 elevated levels of Hg were observed in surface sediments and in the water directly adjacent to the site. The objectives of this study were to: 1) evaluate the extent/concentration of Hg in the downstream floodplain, and 2) evaluate the fate of legacy floodplain Hg after deposition. Evidence for Hg releases during operation of the facility were confirmed by dating an upland (non-floodplain) soil ~4 km downstream using short-lived fallout radionuclides, 7Be and 210Pb. Mercury concentrations in the soil increased significantly during chlor-alkali production in the early 1900's and peak just before decommissioning in 1962 – most likely from Hg release to the atmosphere from the facility and localized atmospheric deposition. Downstream floodplain sediments contain significantly elevated levels of Hg relative to upland soils and this is most likely due to fluvial input of particle-bound Hg from the site. Mercury concentrations are highest in bankfull floodplain sediments, reaching up to 10 µg/g as far as 5 km downstream of the site and remain elevated relative to background levels up to ~15 km downstream. The concentration of Hg in sediment profiles varies as a function of depth as well as distance from the river channel as shown by 13 floodplain transects. Generally, Hg inventories increase from the channel edge with increasing distance from the channel until the edge of the bankfull floodplain where Hg inventories peak and then slowly decrease with increasing distance from the channel. Sequential extractions indicate that Hg in near channel sediments consists of organically-bound Hg(II) as well as a significant fraction comprised of inorganically-bound Hg. In all transects, the proportion of inorganically-bound mercury increases with depth. Soil pore water sampling also indicates a strong temporal variation in the floodplain; pore water Hg concentrations spike during snowmelt runoff and then decay through the summer. Our results suggest that the potential for contaminated floodplains to be a source of Hg to downstream ecosystems will strongly depend on hydrological and biogeochemical processes occurring in the floodplain. This diversity in potential may also indicate similar diversity in future risk of Hg mobilization due to climate change.

TO-077

IMPACTS OF THE MERCURY AND OTHER EMISSIONS FROM THE SMELTER AT FLIN FLON (MANITOBA, CANADA) ON LAKE ECOSYSTEMS: RESPONSES TO SMELTER CLOSURE

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The Flin Flon (Manitoba, Canada) copper-zinc smelter, constructed in the late 1930s, was a major mercury (Hg) and other metals emitter, e.g., an estimated 20 tonnes/yr of Hg were released to the atmosphere in the late 1970s and early 1980s. Studies conducted at that time showed that Hg, copper (Cu), cadmium (Cd), and zinc (Zn) exceeded CCME Probable Effects Levels for sediments in several lakes within 8 km of the smelter and did not approach baseline concentrations until ca. 70 km distant. However, Hg concentrations were exceptionally low (0.04-0.10 µg/g) in 525-mm Northern Pike (Esox lucius) in lakes closest to the smelter with highest concentrations (0.70-0.73 µg/g) in two of four lakes 75-85 km distant; these lakes were slightly acidic (ph 5.9-6.1). Low Hg concentrations in pike close to the smelter were attributed to the inhibition of Hg methylation by metals at toxic concentrations and/or selenium (Se) interference with Hg uptake. Metal emissions subsequently declined with improvements in smelter design and then closure in 2010. Our study, conducted over 2008-2015, is investigating Hg biomagnification in lake food webs, with a focus on Northern Pike. Despite reductions in metal emissions, Cd, Hg, Cu, Zn, and Se concentrations in lake sediments close to the smelter are 1.4-2 higher and in distant lakes 1.1-2.0 times higher than in the early 1980s; immense metal reserves that remain on the landscape continue to be a metal source to these lakes through re-emission and runoff. Hg concentrations in 525-mm Northern Pike in two lakes close to the smelter were higher (0.15-0.49 µg/g) than in 1982 possibly because metals have become less toxic with chemical weathering of metals bound to particulates in the watershed and lake. Percent methyl Hg, a measure of Hg methylation rates, was 2-3% and similar to that observed in lakes (2-6%) in the Thompson smelter area to the east where sediments are not contaminated with metals. Hg concentrations have shown smaller increases (to 0.72-0.92 µg/g) in 525-mm pike in more distant lakes with increases possibly related to warming trends and/or changing water chemistry; pH has increased (mean 7.5) possibly suggesting a reduction in acidifying emissions. Pike condition factor was similar in 1982 (0.68±0.13) and 2008-2016 (0.68±0.08) as was age (5-7 yr) with no differences between metal contaminated and distant lakes suggesting no or little smelter impact on pike growth rates and longevity. Overall, our study shows that despite reductions in smelter mercury emission rates, mercury concentrations in Northern Pike show no evidence of decrease.

TO-078

EVALUATING THE IMPORTANCE OF LEGACY SEDIMENT AND SURFACE WATER LOADING ON MEHG BIOACCUMULATION IN A SULFATE-IMPACTED FRESHWATER ESTUARY

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Mercury bioavailability and bioaccumulation was investigated in the St. Louis River Estuary (SLRE), a shallow (1-3 m) freshwater estuary at the mouth of the largest tributary to Lake Superior. Fish and other benthic invertebrates in the SLRE contain some of the highest levels of methylmercury (MeHg) in the region and are significantly elevated compared to the upstream river and Lake Superior. The upstream river receives large sulfate loads from iron mining, while the lower estuary contains some sediment with elevated mercury from legacy contamination. Also, the SLRE is one of many great lakes coastal wetlands that experiences significant seiche activity, which dilutes river flow in the lower estuary with low-MeHg water from Lake Superior and increases mixing of riparian backwater embayments with river water. The combination of these factors creates a unique setting in which the importance of surface water and sediment as sources of MeHg to the food web cannot be easily discerned. MeHg concentrations in benthic macroinvertebrates were compared with paired sediment and water samples from estuary sites across a spatial gradient of sediment THg and MeHg concentration. Carbon and nitrogen stable isotopes in predator fish tissue show unambiguously that fish feeding in the upper reaches of the estuary have higher MeHg than those feeding in the lower portions of the estuary or Lake Superior. Smaller Hexagenia had higher %MeHg than large Hexagenia and length-corrections were used to investigate spatial patterns and relations with sediment. Linear regressions comparing MeHg in Hexagenia larvae with MeHg in sediment did not reveal a significant relationship and a classification and regression tree model was used to interpret relationships between Hexagenia MeHg and sediment MeHg, carbon, and sulfur. Surface water MeHg concentrations varied seasonally, consistent with patterns in the upstream river, but showed some spatial patterns, likely related to demethylation, seiche-driven dilution and internal MeHg loading. Preliminary results suggest that legacy sediments and internal loading contribute a relatively small fraction of MeHg loads to surface waters of the SLRE, particularly under high flow conditions; however, the importance of near-shore, high carbon MeHg production zones and legacy mercury mobility needs to be more fully understood to effectively target management efforts aimed at minimizing human and ecosystem Hg exposure.

TO-079

METHYLMERCURY QUANTIFICATION IN A CONTAMINATED AGRICULTURAL FLOODPLAIN OF SWITZERLAND USING HPLC-ICP-MS

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The historical use of mercury (Hg) by an industrial plant in the town of Visp, Switzerland has resulted in Hg contamination of soils and sediments in this region. From 1930 to 1976, Hg was utilized as a catalyst for acetaldehyde production, and the Hg-containing wastewater was discharged into an open channel canal which flows along an agricultural floodplain and then converges with the Rhone River. Current estimates indicate that approximately 50 to 60 tons of Hg were released into the canal. Following this, canal sediments were dredged and re-distributed as soil conditioner for agricultural fields and private gardens, resulting in widespread Hg contamination in soils and canal sediments within the affected floodplain. To better understand the distribution and fate of this Hg, soils and sediments within this region were collected and analyzed for total Hg and methylmercury (MeHg) concentrations. Total Hg was quantified by acid digestion and ICP-MS. MeHg was quantified using the following procedure: (i) a combined hydrochloric acid-dichloromethane extraction to release Hg from the soil and sediment matrices and to extract MeHg species to the organic dichloromethane phase; (ii) an aqueous back extraction step to transfer the MeHg to a L-Cysteine solution (0.1% (w/v) L-Cysteine); and (iii) further separation of inorganic Hg(II) and MeHg species using HPLC and quantification of MeHg using ICP-MS (detection limit: ~1 μg/kg). Total Hg concentrations ranging up to 28 mg/kg were detected in agricultural soils adjacent to the canal. Total Hg concentrations decreased with increasing distance from the canal (up to 40 m), and with increasing soil depth (0 to 50 cm). MeHg concentrations up to 7.8 μg/kg were quantified in the soil samples. Our data indicated that MeHg concentrations ranged from < 1 to 3.2 μg/kg, and did not change significantly with distance from the canal or with soil depth, except in one case (depth: 20 cm, distance from canal: 5 m) where 7.8 μg/kg MeHg was detected. MeHg/total Hg ratios for all samples were ≤ 0.08 %. Ongoing analyses include quantifying MeHg concentrations in sediment grab samples as well as in sediment cores along the length of the canal, and total organic carbon, total carbon, nitrogen and sulphur analyses to determine the source of MeHg and soil/sediment properties which may be correlated with MeHg and Hg methylation processes.

TO-080

IMPACTS OF HYDROELECTRIC POWER PLANT ON MERCURY EXPOSURE OF RIVERINE COMMUNITIES IN AMAZON BASIN.

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Hydroelectric power accounts for 83% of global electricity generation in Brazil. It is estimated that in 2030, electricity consumption in Brazil will be between 950 and 1,250 TWh/year, much higher than the current consumption of around 400 TWh/year. A great expand capacity is underway and it will be concentrated in the Amazon Basin where the high mercury load in the ecosystem is known and distinct social and environmental conditions need to be carefully analyzed, due to the potential to cause environmental, social and health impacts of great magnitude. The scale of the impacts is related to the type of technology used by the hydroelectric plant. In our case, the Madeira hydroelectric power plants used run-of-river type without formation of large reservoirs, consequently, with smaller flooded areas. The main aim of the present study was to assess the health impact of mercury exposure of the riverine communities in the phase of pre and post-impoundment of the hydroelectric reservoir in the Madeira River in the Amazon Basin. Traditional diet of riverine communities in Amazon basin is rich in fish that is an important source of protein. It is well known by the literature that flooded reservoir provide significant MeHg production peaks within the first 5 years in the aquatic environment and gradually declined back to baseline over several decades. In our case study of the hydroelectric power plant in the Madeira River, the health impact assessment of the mercury exposure of riverine communities had start before the pre-impoundment (2009-2011). For the phase of the post-impoundment (2014 to 2016) a longitudinal and a transversal studies were carried out for the influence area of the hydroelectric power plant. The results showed that the hair Hg levels were different for the upstream and downstream riverine communities for the two periods (pre and post-impoundment). The results of the post-impoundment (2009-2011) showed that the group of adults (16 years of age or older) the average concentration of Hg in hair was 9.4 ± 10.6 µg/g, with a minimum of 0.3 µg/g and a maximum of 66.8 µg/.g. In the period of post-impoundment 2014-2016, the average concentration of mercury in hair was 5.9 ± 6.1 µg/g, with a minimum of 0.1 µg/g and a maximum of 32.5 µg/g. The median in both periods was 5.7µg/g-1 and 4.2µg/g, respectively. The difference between the periods was statistically significant (p-value = 0.008).

TO-081

MERCURY CONTAMINATION FROM THE HISTORIC HATTING INDUSTRY IN WESTERN CONNECTICUT, USA

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The saying mad as a hatter stems from the medical condition of hatmakers who commonly used mercury nitrate in the preparation of felt for hats. Danbury, Newtown and Norwalk were centers of hatmaking in Connecticut in the 1800-1900s, with production of > 1million hats/year around the turn of the century. Much of that Hg has remained in the local uplands near the former hatmaking plants (68 plants in Danbury alone) and in the sediment of the rivers draining these areas (Still River, Housatonic River, Norwalk River). Sediment cores from a cove along the Still River carry up to 100 ppm Hg and river bed sediment of the Still River and Housatonic River has several ppm Hg. Sediment cores from river coves and marshes are analyzed for 210Pb, 14C, Hg, bulk dry density, and TOC and these dated core records provide accumulation rates of Hg for the last 100-200 years. The onset of Hg contamination coincides broadly with the beginnings of the local hatmaking industry and most profiles show a decline since the mid 1900s. Mercury use in hatmaking was halted in 1941. Ultimately, much of the hatting Hg ended up in Long Island Sound (LIS). Mass balancing the Hg input from the Housatonic River into LIS suggests that 25 to 35% of all Hg in LIS stems from the hatmaking industry. This Hg is spread through tidal and current activity widely throughout the Sound. During periods of intense rainfall, Hg-rich sediment is carried through the rivers directly into the Sound, leaving thin Hg-enriched event layers in the stratigraphic record. We compare the LIS Hg records with lake records from Block Island, RI, which we interpret as representing largely in situ atmospheric deposition. Marshes in central LIS remote from the source area and river inputs still carry a strong imprint of this legacy Hg from the Western CT hatmaking industry. This old Hg can become reduced in LIS and then potentially vented back into the atmosphere as Hg(o).

TO-082

IMPLICATIONS OF BENTHIC MACROINVERTEBRATE COMMUNITY STRUCTURE ON MERCURY BIOACCUMULATION IN FISH

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Mercury is a globally important contaminant which is of particular concern in stream systems. Because the consumption of contaminated fish is the most significant source of mercury (Hg) exposure to humans, regulatory guidelines that focus on the protection of human health require monitoring of both aqueous and fish tissue Hg concentrations at contaminated sites. However, because Hg is predominantly accumulated in fish via dietary rather than aqueous exposure, the link between aqueous Hg concentrations and concentrations in fish is not always straightforward, confounding remediation efforts at contaminated sites. Benthic macroinvertebrates can often comprise a major portion of fish diets and can therefore be important in the trophic transfer of bioaccumulative contaminants like Hg to fish. Benthic macroinvertebrate communities are commonly monitored in streams as an indicator of water quality, and while these community surveys do not provide direct information on Hg bioaccumulation, they can provide information relevant to understanding food web dynamics, and therefore Hg bioaccumulation, within a given system. Here, we examined changes in the invertebrate community over 30 years at two sites in East Fork Poplar Creek, a Hg-contaminated stream in East Tennessee, to explain why Hg concentrations in resident fish have not decreased in response to remediation activities that have been successful in decreasing aqueous Hg concentrations. We used the density and biomass of the major functional feeding groups in the invertebrate community, in conjunction with current efforts to quantify mercury inventories within the biota of this stream, to create a food web model to predict the most important factors leading to elevated Hg concentrations in fish. Bioconcentration factors (BCFs) were calculated for macroinvertebrate functional feeding groups using Hg concentrations in macroinvertebrates relative to aqueous Hg concentrations from 2013-2016. The BCFs were then applied to historical aqueous Hg concentrations to back-calculate Hg concentrations in the macroinvertebrate community over time. The diet of rock bass, the target fish species, was estimated at a given time period based on relative biomass and densities of macroinvertebrates at that time to calculate a weighted concentration for Hg trophic transfer to this species. Our results suggest that observed increases in the benthic macroinvertebrate community species diversity over time (i.e. longer food chain lengths) could explain why Hg bioaccumulation in fish has not changed despite substantial reductions in Hg loading into this stream.

3d: Engagement of communities impacted adversely by environmental mercury pollution

TO-083

ELEVATED MERCURY EXPOSURE IN NATIVE POPULATIONS IN THE SOUTHERN PERUVIAN AMAZON

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The Amazonian region of Madre de Dios in southeastern Peru has a extensive and highly active artisanal and small scale gold mining (ASGM) sector which uses mercury to concentrate gold found in alluvial sediments. Due to poor mining control practices, considerable amounts of elemental mercury are released to waterways, where it is biochemically converted to highly bioavailable methylmercury (MeHg), which enters the aquatic food webs and accumulates in river fish. River fish is the primary protien source for tens of thousands of native persons living in remote traditional settlements across the region. Elevated levels of MeHg exposure have previously been documented in Madre de Dios. However, no previous study has focused on MeHg exposure specifically native populations across the region. This cross sectional study focuses on hair mercury concentrations of persons in twelve native communities representing four different ethnicities in different stages of cultural contact across the region. Some of the communities were actively engaged in artisanal mining. Hair samples were collected from 306 persons between the ages of 1 and 89 as part of the Carnegie Amazon Mercury Project. The hair samples were analyzed for total mercury (THg) concentration, an established indicator of MeHg exposure. A corresponding survey was administered (when possible) to collected dates on potential risk factors including age, location, sex, frequency and type of fish consumption, and history of mining work. Mean hair THg in all native community populations were significantly elevated compared to non-native populations in Madre de Dios. A majority of individuals in the study population had THg levels above the U.S. EPA and WHO reference values. One native community in particular, had the highest mean community hair Hg values yet reported in the Peruvian Amazon. Study participants who reported consuming fish had significantly higher THg exposure than those who did not consume fish. Segmental hair analysis on a subset of the sample looked at Hg exposure over a 3 year period and confirmed fish consumption as the principal factor in hair THg concentrations.. Study participants who reported having worked in mining had significantly higher Hg exposure than participants with no history of mining. In general, there was no association between hair THg and age or sex, through some relationships were found between age and hair THg in certain highly exposed communities. The results of the current study are consistent with the findings of previous human Hg exposure studies from the region, indicating that an urgent public health risk due to artisanal mining related mercury exposure exists for native communities in Madre de Dios.

TO-084

INFORMING SENSITIVE POPULATIONS CONCERNING HEALTHFUL SEAFOOD CONSUMPTION

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Our seafood safety initiative has worked over the past 2 decades to help pregnant or nursing women, and women who will become pregnant to make informed decisions concerning their consumption of seafood. Our goal is to encourage women to: consume 8-12 ounces of seafood pre week; consume species which provide healthy fats; avoid consuming species which are higher in mercury or PCBs; and avoid raw seafood when pregnant or feeding young children. To accomplish this goal, we have developed free educational materials which have been deliver using: a website (www.fish4health.net); iPhone and Android apps (fish4health); and a seafood safety wallet card. The seafood safety wallet card has been widely distributed (over 1 million) across the U.S. and adopted by State health departments in Florida and Indiana. Focus groups (conducted independently at URI) reported that the wallet card gave women the confidence to safely consume seafood by eliminating confusion surrounding these products. Recently, we recruited pregnant women from a WIC clinic to assess, through online pre- and post-training surveys, the impact of the wallet card on the subjects knowledge and attitudes concerning their seafood choices. We also conducted a 2 month, post-, post-training survey to assess the impact of the wallet card on subjects consumption behavior.

TO-085

"WHEN CAN WE EAT THE FISH?": DESIGNING AND PRACTICING COMMUNITY-ENGAGED, -DIRECTED RESEARCH IN AN INTERDISCIPLINARY, MULTI-JURISDICTIONAL MERCURY INVESTIGATION

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Addressing global socio-ecological problems such as mercury contamination requires new methods for doing collaborative research and creating mutually beneficial projects between researchers, policy institutions, and community members.This paper focuses on the ways collaborative research has been facilitated in Lake Superiors Keweenaw Bay in the interdisciplinary research project titled Managing Impacts of Global Transport of Atmosphere-Surface Exchangeable Pollutants (ASEPs) in the Context of Global Change at Michigan Technological University. Specifically, it highlights the use of strategic research design and practice in participatory research to identify questions of interest to affected communities and policy actors. By engaging in forums such as workshops, focus groups, and talking circles, when can we eat fish? emerged as the priority mercury concern among participants. These forums were carefully structured in an effort to level the playing field between differing research participants including investigators from social and natural science disciplines, multi-jurisdictional organizations, and Indigenous and non-indigenous community members. Aims for implementing participatory forums were to enhance dialogue on the global transport of toxic compounds (including mercury) and their management in the Great Lakes, to increase understanding of contamination issues from diverse perspectives, and to develop future collaboration opportunities between the research team, organizational partners, and community members in Keweenaw Bay. As a community-directed initiative, when can we eat the fish? significantly transitioned the trajectory for the research to be conducted. Community concerns became developed into an interdisciplinary scientific inquiry, and further, influenced the specific factors chosen to answer this question concerning safe fish and mercury contamination. The conclusion emphasizes the value of explicitly addressing power dynamics in research design and practice, and argues that such forums are crucial for facilitating the type of research that is necessary to address problems as complex as those associated with global mercury contamination. It serves as a reminder that building relationships across disciplines, jurisdictions, and communities is an important pathway toward integrating mercury research and policy in a changing world and thus creating a more sustainable socio-ecological future.

TO-086

MERCURY CONTAMINATED FISH FOR THE NARRAGANSETT TRIBE: COSTS AND BENEFITS

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Fishing and fish consumption among Indigenous populations are culturally and economically vital activities, as well as important determinants of health. While seeking to protect the public from harmful health impacts, fish advisories do not take into account the impact of the absence of fish on Indigenous culture. Conversely, continuing the tribal fishing traditions in communities impacted by environmental contamination has the potential to place tribal members at increased risk for health impacts from these contaminants, specifically mercury (Hg) and polychlorinated biphenyls (PCBs). However fish is an important source of protein, selenium (Se), and omega-3 polyunsaturated fatty acids, which have been shown to have beneficial effects for preventing cardiovascular disease and mortality. In addition, it is known that selenium can inhibit the absorption of methylmercury. In order to help one Native American community assess the impacts of environmental contamination, and to facilitate informed decision-making regarding fish consumption and fish contamination in Tribal waters, the Namaus Project was developed as a collaboration between the Narragansett Tribe and the Brown University Superfund Research Project. Addressing complex environmental contamination requires

assembling multidisciplinary teams of academic researchers, state and federal regulators, Tribal government officials, educators, artists, and community members of all ages. To accomplish this, and make this a truly community based participatory research (CBPR) project, Namaus Project team members have worked as knowledge brokers, working to collaborate across multiple stakeholder groups in order to integrate scientific knowledge with cultural knowledge, creating multidirectional knowledge exchanges between Traditional Environmental Knowledge bearers and scientists and regulators. This contributes to building the capacity of the Narragansett Tribal government and its members for informed decision-making and participation in Tribal environmental health policy and regulatory formulation. To accomplish this, Namaus team members gathered and tested fish samples from tribal ponds; worked with consultants to establish heritage rates of fish consumption based on historic and ethnographic data; and hosted focus groups with Narragansett tribal members in order to learn more about the role that fish and fishing have had in tribal culture, and the impact that the diminishment of fishing has and will have on health and culture of Narragansett people. This presentation will describe the process by which this collaborative project was established, the quantitative and qualitative results of the fish sampling and focus groups, and plans going forward to include artists and cultural programs in developing messaging materials for community members on the costs and benefits of fish consumption.

TO-087

MERCURY EXPOSURE ASSESSMENT IN YANOMAMIS INDIGENOUS POPULATION FROM THE BRAZILIAN AMAZON

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Mercury contamination due to artisanal and small scale gold mining (ASGM) has been studied in several locations in the the Brazilian Amazon, reporting a wide range of Hg hair levels in native populations. However, exposure studies are rare in the Brazilian state of Roraima which is home to the Yanomami indigenous people. Recent expansion of ASGM activity in the Yanomami Community Reserve has increased public health concerns in the native community and led Yanomami community leaders to request the Brazilian Ministry of Health's National School of Public Health to conduct a mercury exposure assessment. The main objective of the subsequent study was to assess hair Hg concentrations of vulnerable groups, women of reproductive age and children less than six-years-old, in two different community locations. Results indicated hair Hg levels were different between the two population locations. Those in Paapiu, an area where gold mining was active during the 1980's but had been significantly reduced, presented lower levels (median 3.2 µg g-1) as compared with the Waikas region (median 5.0 µg g-1), which has experienced a resurgence of ASGM since 2013. Within the Waikas region, the small community of Aracaca, reported to participate directly in gold mining showed the highest Hair Hg levels (median 15.5 µg g-1). It was concluded that ASGM related Hg was the likely source of Hg exposure for these communities. Also, further studies in other communities of the study area was recommended, as well as an intervention to stop ASGM in Yanomami territories. Health impact of Hg in these communities are still unknown. Study results were presented and explained to the studied group. The indigenous leaders asked the study researchers to present the study findings to the federal environmental and health ministries. Because these isolated native populations are totally dependent on their environment, ecosystem contamination by ASGM related mercury is likely to cause negative health impacts and put their continued survival at risk. ASGM activities in the Amazon should be regulated to reduce and control the impact on this ecosystem. It is also important to raise awareness that Amazonian indigenous communities are essential for the conservation of this area.

TO-088

EDUCATION AND AWARENESS-RAISING TO PREVENT HUMAN EXPOSURE TO MERCURY: ONGOING EXPERIENCES IN MADRE DE DIOS, PERU

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The region of Madre de Dios in the southeastern Peruvian Amazon, rich in biodiversity and ancestral Amazonian cultures, has faced for several decades one of the most serious extractive pressures due to the rise in the price of gold, obtained through artisanal and small-scale gold mining activities, which causes a release to the environment of up to approximately 35 MT Hg/year, with the consequent threat to the health of people, mainly women of childbearing age, children and indigenous peoples.

Although a remarkable emphasis has been given in the last years by the national and international press, as well as by several civil society institutions and by some national ministry, to raise awareness and draw attention to this problem; Very few efforts have been made to influence in an effective and sustainable way the generation of policy and concrete actions to prevent exposure to the risk of mercury contamination in the entire population of Madre de Dios.

Since 2010, the concertation and coordination of local actors decided to influence and work on educational and awareness-raising actions in the general population and in the local education system as strategies to approach and design and implement local actions and prevention policies to reduce Risk of exposure to pollution.

Specifically:

- **A.** Information fairs in squares and fairgrounds.
- **B.** Training of teachers, to approach the subject in classroom.
- **C.** School fairs inside schools and public squares.
- **D.** Development of posters, leaflets, methodological guides for training teachers and health promoters.
- **E.** Research forums, drawing the attention of authorities.
- **F.** Elaboration and distribution of spots: audio and video.

As a result:

- **A.** Change in fish consumption patterns in the city of Puerto Maldonado, increasing the consumption of species with lower risk of contamination, and strengthening the development of fish farms.
- **B.** Training of approximately 700 public officials in the education, health and other sectors.
- **C.** Mastery of the approach of the subject in the education sector: from addresses, specialists, teachers, students and parents, through the implementation of the Curriculum by emergency.
- **D.** Adoption and adaptation of the theme by the staff of the Regional Directorate of Education and teachers.
- **E.** Results of scientific research serving as inputs for the issuance of national standards (Supreme Decree No. 034-2016-PCM and Supreme Decree No. 054-2016 PCM) and facilitating the action of local authorities on the issue (Multi-sectorial Operation for the Eradication of Gold buying and selling shops that re-fired near the main market of the city)
- **F.** Trend in the change in the discourse of politicians and mining leaders, who begin to promote and adopt new technologies that do not use mercury

TO-089

CASE STUDY OF A MULTI-FACETED PUBLIC OUTREACH PROGRAM FOR A MERCURY-IMPACTED RIVER

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An innovative multi-faceted public outreach program has been developed to promote community education, involvement, and feedback for a mercury (Hg) impacted river system in central VA, USA. Between 1929 and 1950, Hg was released into the South River, resulting in Hg concentrations in soil, sediment, surface water, and biological tissues above regional background levels. Hg concentrations in edible fish tissues have led to fish consumption advisories affecting approximately 140 river miles along the South River, South Fork Shenandoah River, and the Shenandoah River. The South River Science Team (SRST) was established in 2001 with a goal to conduct studies to better understand the distribution of Hg in the affected waterways and associated floodplains as well as reduce Hg bioavailability to ecological receptors. As part of the SRST, a multi-faceted public outreach program was created to effectively communicate the presence of Hg in the river system, primarily the fish consumption advisory, to the community, and to promote collaboration with community stakeholders regarding the proposed remedial approach.

A critical aspect of the outreach program is the effort to adapt as new populations in the area are identified or as demography in the area changes. To effectively communicate the consumption advisory to the growing Spanish, Arabic, and Kurdish-speaking populations in the area, the SRST has partnered with James Madison Universitys Promotores de Salud Program. Fish consumption advisory information is available in English, as well as in Spanish, at frequently used river access locations. Additional SRST materials are available at the SRST office, located in downtown Waynesboro, Virginia as well as on the SRST website. Community relations take place through a number of different outlets, including, Waynesboros annual Riverfest, Student Day, and Fly Fishing Festivals, school outreach activities, media briefings, and river-use surveys conducted by Virginias Department of Game and Inland Fisheries.

The remediation advisory panel was established to facilitate communication between the stakeholders and community groups prior to and throughout the proposed remediation processes. The remediation advisory has representatives from city and state agencies, community organizations, and local interest groups. Various meeting formats are held regularly to communicate with landowners potentially affected by remedial activities, city representatives, and the general public; these meetings are intended to not only keep the public informed of remedial plans and activities, but also to solicit feedback from the community.

TO-090

MENTAL MODELS OF MERCURY RISK AMONG SOUTH FLORIDA ANGLERS

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Traditional approaches to studying and improving environmental reasoning and decision-making processes have tended to adopt an information deficit model, assuming either explicitly or implicitly that if individuals are provided with scientific information in a form which they can understand that they will make decisions consistent with that information. This rationalist model of human behavior has proven inadequate in explaining a recurrent observable gap between what people know and think about the environment, and how they act upon this knowledge; in other words, even when members of the general public accurately know discrete facts about things like environmental risks or hazards, they frequently take actions inconsistent with that knowledge. This phenomenon that has been well-documented by researchers examining public compliance with mercury advisories for fish. One of the most promising theoretical approaches in examining how people understand and interact with environmental systems and explaining the gap between knowledge and behavior examines peoples mental models of the environment. Developing largely out of the interdisciplinary field of cognitive science, it proposes that human beings reason and make decisions by constructing and referencing internal, simplified models of the real world. Under this theory, simply providing additional information to individuals may prove ineffective in improving decision-making, particularly as mental models are resistant to change. This paper describes mental model theory in a risk analysis context, and applies it to investigate how recreational and subsistence anglers in the Miami-Dade canal system understand and make decisions regarding mercury risk, and howunderstanding those models can inform better risk management and risk communications from environmental and health managers. Using semi-structured interviews, participant observations, and a review of mercury advisory communications, it examines participants nave mental models of mercury cycling and exposure, and offers potential communication strategies to change or account for these models and improve decision-making about mercury risk.

4a-2: Informing the implementation of the Minamata Convention: the role of scientific assessments

TO-091

HUMAN BIOMONITORING OF MERCURY TO TRACK THE EFFECTIVENESS OF THE MINAMATA CONVENTION

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The Minamata Convention on Mercury is a multilateral environmental agreement that obligates Parties to reduce or control sources of mercury pollution in order to protect human health and the environment. Evaluating the effectiveness of the Convention (as required by Article 22) is a crucial component to ensure that it is meeting this objective. The purpose of this talk is to describe human biomonitoring of mercury, and how this represents a scientifically robust, straightforward, and potentially cost-effective approach to track the effectiveness of the Convention over temporal and spatial scales. First, I will discuss the pros and cons associated with using accepted biomarkers of Hg exposure (hair, blood, and urine) and associated exposure assessment strategies (e.g., surveys). Second, I will describe national biomonitoring programs that exist in countries including the U.S. (via NHANES), Canada (via CHMS), Germany (via HBM), and Korea (via KNHANES), and describe how these programs have enabled countries to establish baselines and reference ranges (at the national and regional level), help set priorities and take action, and track changes over time as part of surveillance efforts. Finally, I will discuss approaches to gauge exposures in vulnerable populations (e.g., dental professionals, small-island nations, ASGM sector). The talk will attempt to articulate challenges and opportunities concerning the human biomonitoring of mercury in the context of the Convention, and portray global patterns.

TO-092

DEVELOPING A GLOBAL KNOWLEDGE MANAGEMENT PLATFORM SOLUTION FOR MERCURY EMISSIONS, FATE AND EXPOSURE DATA

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The UNEP Minamata Convention on Mercury, signed in 2013 and to date ratified by 35 countries with 128 signatories, recognizes that mercury must be managed at a global scale. To develop regional and local bases for evidence-based management decision-making requires the ability to capture, synthesize, analyze and visualize data at varying spatial scales and time frames. It is essential to facilitate understanding among stakeholders and regulators of how emissions reductions and site-specific projects associated with implementing provisions of the Convention affect the broader exposure and risk profiles of human populations and ecosystems.

This project, which started in 2015, attempts to design and populate a centralized platform, deployed via UNEP Live, for data upload and download as well as knowledge sharing through information synthesis and facilitation of Communities of Practice comprising scientific expert and critical stakeholder groups. The term knowledge sharing is a deliberate attempt to move beyond traditional web-based delivery of quantitative but uninterpreted information. This will be done through user-mediated requests for data synthesis and visualization as well as implementation of data protocols and delivery of meta-data as a component of shared output.

A demonstration pilot project, using a selected set of data on total mercury in billfish and food consumption advisories, was recently completed. In order to understand and anticipate user needs for the platform, a global survey was conducted. Essential findings of the survey will be described. A key element of knowledge creation is incorporation of pre-set or user-defined ways to provide insight and answers, not just data. The foreseen critical elements of a larger production scale deployment of the platform will also be presented. A particular focus will be on connecting prospective users with the information and data providers through a mediated Communities of Practice. A brief vision of future planned work will be provided.

TO-093

A META-ANALYSIS OF FISH MERCURY CONCENTRATIONS IN SOUTH AMERICA: IDENTIFYING PATTERNS, TRENDS AND HOTSPOTS FOR FUTURE BIOMONITORING RELATED TO THE MINAMATA CONVENTION ON MERCURY

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The Minamata Convention was established to protect humans and the environment from exposure to mercury. Implementation of the Convention will rely on signatory countries adopting a series of measures to limit the amount of Hg used in commercial and industrial practices, reduce emissions and releases of Hg, and establish legislation and trade policies to further reduce and restrict the amount of Hg available on the global market (UNEP 2013).

The Conventions success at achieving its goal of protecting human health and the environment can be assessed using a variety of short-, medium- and long-term metrics that monitor compliance with stipulations set forth in the Convention (Evers et al. 2016). The Convention also recognizes the important role that monitoring environmental Hg concentrations will have in assessing its long-term effectiveness. Articles 19 and 22 of the Convention specifically address the importance of biomonitoring to evaluate spatial and temporal patterns and trends of Hg in the environment at geographically relevant scales.

Here we present data on fish mercury concentrations from South America to identify patterns and trends in environmental Hg concentrations at the continental scale. The Web of Science was used to search for published literature using the search terms mercury AND fish AND [country name]. Additional searches were conducted using Google Scholar. All literature published prior to April 2016 were collected for inclusion in the database resulting in more than 200 peer-reviewed sources. At least one peer-reviewed source was identified from each country with the exception of Guyana and Paraguay.

To-date, our database includes results from 110 peer-reviewed sources representing 24,550 individual fish tissue samples. Samples reflect environmental Hg concentrations in more than 240 sites within 100 different major waterbodies across the continent. Mercury concentrations ranging from below detection limit to 4.4 parts per million (wet weight) are reported in 403 different species representing 227 different genera. The most commonly sampled taxa include species within the Serrasalmus (piranhas), Hoplias (tigerfishes) Pseudoplatystoma (sorubim catfishes) and Odontesthes (silversides) genera. Subsequent analysis will incorporate spatial data on known point sources of mercury, ecosystem types, geology and hydrology to better understand abiotic variables that influence environmental mercury concentrations. Ultimately, these data provide a baseline for identifying biological mercury hotspots of concern for human and ecological health at the continental scale. This baseline will help prioritize future biomonitoring efforts to best evaluate the long-term effectiveness of policy decisions related to the implementation of the Minamata Convention.

TO-094

ENVIRONMENTAL MONITORING DURING THE U-864 COUNTER FILL INSTALLATION

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The wreck site of the World War II submarine U-864 is located at 160m depth near the island of Fedje on the west coast of Norway. The submarine carried 67 tons of metallic mercury. The sediment surrounding the wreck is heavily contaminated, and steel containers holding the cargo is still considered to be present inside the wreck. In 2015 it was decided to place a counter fill in front of the bow section which has been found to rest on a slope with unstable sediments. The Norwegian institute for water research (NIVA) was assigned to be responsible for implementation of the monitoring program required during the operations in May-June 2016, where objectives were to minimize spreading of mercury during installation of the counter fill material and to estimate the total amount of mercury transported out of the working area.

The counter fill covered a 200m by 60m area immediately north of the bow section of the wreck. Five landers measuring turbidity at 1,5m and 10m above sea floor surrounded the area. Data values were transmitted every five minutes through a connected buoy and Iridium satellite, presented visually on a website, and used to generate automatic alarms (when turbidity was >10 NTU). Alarms enforced water sampling from the designated Environmental Monitoring Vessel (EMV, Siddis Mariner), and the content of mercury was analyzed at the onboard laboratory within 30 minutes to a detection limit of 0.5 ng/L. Mercury levels above the threshold would trigger construction stop and mitigation actions. Daily routine sampling was done using hydrographic instruments for salinity, temperature, and turbidity (CTD) and LISST which measures particle size distribution. Analyses of mercury and grain size was performed on particles collected in sediment traps and vibrocore samples.

Mercury concentrations in the water samples never exceeded 1.3 ng/L, much less than the predetermined limit of 50 ng/l for initiation of mitigating actions. Operations were never stopped due to risk of mercury spreading. Estimated total flux of 34 g of mercury for the entire operation was two orders of magnitude less than the predetermined acceptance criterion of 3 kg. All the data collected through mercury analyses, CTD, LISST and the online monitoring provided information contributing to a more complete understanding of the mechanisms controlling the spreading of mercury during such operations. All relevant data consistently confirmed that the particle clouds observed was dust from the counter fill material with negligible contributions from resuspended sediments.

TO-095

VINVERSION APPROACH TO VALIDATE MERCURY EMISSIONS BASED ON BACKGROUND AIR MONITORING AT THE HIGH ALTITUDE RESEARCH STATION JUNGFRAUJOCH (3580 M)

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The key objective of the Minamata Convention, a UN treaty designed to protect human health and the environment from adverse effects of mercury, is the reduction of mercury emissions. To assess the effectiveness of the convention in the future, better and independent constraints about the current mercury emissions is a premise. Existing inventories for anthropogenic mercury emissions use a bottom-up approach, where the releases are estimated using activity data and activity-specific release factors. In this study an alternative top-down approach, based on measured atmospheric mercury concentrations, is applied to quantify European mercury emissions. Gaseous elemental mercury (GEM) measurements were conducted at the remote high-altitude monitoring station Jungfraujoch, situated at 3580 m.a.s.l. in the Swiss Alps. Using a Lagrangian Particle Dispersion Model we backtracked the air masses arriving at the measurement site and established the source-receptor relationship between our measurement location and the source domain. By the means of Bayesian inversion we then were able to quantify spatially resolved European mercury emissions. We found mercury emissions to be higher by 17% compared to existing inventories. While for some areas we obtained similar or even lower estimates other regions in Greece, Spain, and Romania have shown much stronger source strength. Overall, stationary combustion, in particular in coal-fired power plants, is found to be the main responsible sector for increased emission estimates. Our top-down study, based on measurements, provides a novel and independent approach to capture mercury emissions. Our investigations help to improve and refine reported emission inventories, and can serve for continued assessment of future changes in emissions independent from bottom-up inventories.

TO-096

ALBATROSSES AS BIOMONITORS OF HG IN THE SOUTHERN HEMISPHERE

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Seabirds are powerful biomonitors of Hg contamination, and analyses of their feathers constitutes an appropriate and non-lethal method to evaluate the levels of Hg exposure in marine habitats. Albatrosses range widely within the Southern Hemiphere where they feed at high trophic levels. Therefore, they appear suitable for monitoring Hg contamination over large spatial scales. Albatrosses are known to present high but variable Hg concentrations. Such variability could be due to the combined effects of their breeding frequency, moulting patterns, and trophic ecology. To determine the significance of various factors (taxonomy, breeding frequency, feeding habitats [δ13C] and trophic level [δ15N]) on Hg concentrations, we used an exceptional data set of 455 individuals from all the species and subspecies of albatrosses breeding in the Southern Ocean and adjacent waters (n = 22). In some species, we analysed Hg, δ13C and δ15N values in different body feathers from the same individuals. As predicted, mean Hg concentrations varied widely (ten-fold) among albatrosses, from means ± SD of 3.8±1.5 to 34.6±12.5 μg.g-1 in the Indian yellow-nosed and Amsterdam albatrosses, respectively. Considering the taxonomy, Diomedea (7 taxa) had the highest Hg levels, followed by Phoebetria (2 taxa) and then Thalassarche (11 taxa). Consequently, biennial breeders (Diomedea and Phoebetria) are more contaminated by Hg than annual breeders (Thalassarche). A general decrease of Hg concentrations was found with increasing latitude (using δ13C as a proxy), with the lowest Hg concentrations in feathers moulted in Antarctic waters, and the highest in those moulted in subtropical waters. The latitudinal effect was verified at the individual level by measuring different feathers from the same wandering, light-mantled and sooty albatrosses. The study shows that albatrosses (and especially Diomedea taxa) are the seabirds with the highest Hg burdens worldwide, and that Hg exposure to predators is lower in antarctic than subantarctic and subtropical latitudes.

TO-097

CLIMATE CHANGES AND POTENTIAL IMPACTS FOR EVALUATING THE EFFECTIVENESS OF THE MINAMATA CONVENTION

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Regulatory assessments of the impacts of mercury (Hg) emissions reductions generally assume constant environmental conditions when evaluating and quantifying benefits of policy actions. By contrast, biomonitoring programs in the field are affected by changing biogeochemical conditions that influence temporal changes in methylmercury (MeHg) concentrations. To develop effective monitoring programs, such effects would ideally be quantified separately from the benefits associated with reductions in anthropogenic Hg emissions. This presentation will discuss and, when possible, quantify the influence of changing ecosystem conditions on MeHg production and bioaccumulation in marine food webs. Changing ocean productivity leads to shifts in phytoplankton community structure and MeHg uptake at the base of marine food webs. Global ecological modeling indicates such effects are most pronounced in the polar oceans. Intra-species variability in MeHg generally increases with age of aquatic biota. Food-web bioaccumulation modeling shows increasing seawater temperatures increases energetic requirements of different fish species leading to elevated MeHg concentrations. Changes in trophic structure by contrast can either increase of decrease fish MeHg concentrations, depending on the initial diet of the species in question. We find these shifts can easily exceed a 20-30% change in most fish species, which is within the range of declines in ecosystem Hg inputs achieved by controls on global anthropogenic emissions. We find sample sizes on the order of hundreds of fish each year are needed to have sufficient power to detect statistically significant changes in MeHg concentrations and such considerations would assist in the design of effective biomonitoring strategies supporting the Minamata Convention.

TO-098

EVALUATING THE EFFECTIVENESS OF THE MINAMATA CONVENTION ON MERCURY: DEVELOPING A BIOMONITORING TOOLKIT

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The Mercury Air Transport and Fate Research Area, a Global Mercury Partnership of the United Nations Environment Programme (UNEP FT), has the overarching objective to increase the understanding of worldwide sources of mercury (Hg) emissions and releases, their transport and fate, and impacts to humans and the environment. As part of the UNEP FT Business Plan, an important objective is to monitor, assess and report on information that can be used as the basis for assessing the environmental and public health benefits and effectiveness of global Hg reductions pursuant to the Minamata Convention on Mercury.

One policy-relevant contribution of the UNEP FT, for use by all Parties, is to develop a standardized and replicable approach for Hg biomonitoring. Our approach is an extension of the currently used UNEP Toolkit for Identification and Quantification of Mercury Releases used for the Minamata Initial Assessment process (currently conducted by over 90 countries). We now propose the development of a Toolkit for the Identification and Quantification of Biomonitoring Needs to be used by Parties for prioritizing next steps for biomonitoring related to national interests and contributing toward evaluating the effectiveness of the Minamata Convention.

The biomonitoring toolkit will use an Excel platform. Such an evidence-based approach is simple, straightforward, replicable and scalable. The premise for the toolkit on Hg biomonitoring is to respond to applicable, policy-relevant questions that will contribute to the needs of Article 22 through methods outlined in Article 19, to evaluate the effectiveness of the Minamata Convention, as well as to help Parties identify and prioritize areas of greatest concern to human health and the environment (i.e., biological Hg hotspots).

Multiple input variables that use existing data from a countrys National Mercury Profile, generated from the Minamata Initial Assessment and other publicly available sources (e.g., national and international), will provide the basis for generating policy-driven outputs, such as mapped models of air, water and biotic Hg concentrations, and when combined with landscape sensitivity variables (e.g., wetlands) biological Hg hotspots of concern can be identified and used to prioritize biomonitoring. Hazard-exposure-receptor models, based on seven input variables and the concept of their combined attributes, will allow biological Hg hotspots of concern for human and ecological health to be mapped and prioritized according to criteria set by a country. Understanding the interaction of biological Hg hotspots with sources of wild food items that are important for human communities will be of highest priority.

1a-1: Atmospheric mercury cycling and transformations: Insights from measurements and models

WO-001

DEVELOPING GLOBAL ATMOSPHERIC MERCURY MONITORING STRATEGIES THAT ARE ROBUST TO CLIMATE VARIABILITY AND CHANGE

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We use earth system and atmospheric chemistry modeling to investigate the implications of climate variability and change on strategies for monitoring the effectiveness of global mercury policy. As the Minamata Convention moves towards the implementation phase, developing strategies for monitoring treaty effectiveness is a science-policy priority. Given that the atmosphere is likely to respond relatively rapidly to policy-related emissions changes compared to other environmental media, atmospheric monitoring strategies are critical. However, atmospheric concentrations and fluxes (wet and dry) are not only influenced by anthropogenic mercury forcing; meteorological variables such as temperature, precipitation, and circulation patterns have implications for mercury chemistry and transport, and resulting observed concentrations and fluxes at monitoring sites. In this work, we assess the potential influence of climate variability and change on ability to detect policy-related anthropogenic changes in mercury emissions.

We simulate atmospheric concentrations and fluxes of mercury using the GEOS-Chem chemical transport model, driven by an ensemble of meteorological fields from the MIT Integrated Global System Model that encompasses a range of initial conditions, climate stabilization scenarios, and climate sensitivities. Using this ensemble, we estimate the distribution of atmospheric concentrations and fluxes consistent with the implementation Minamata Convention, under possible climate futures (mid-century and end of century). We find that more than 10 years of data are required to detect anthropogenic signals in mercury, given the magnitude of current and future climate variability when relying on a single monitoring metric (e.g., wet deposition); however, combining co-located flux and concentration measurements can reduce this time of emergence. To better understand what drives this climate-related variability in atmospheric mercury concentrations and fluxes, we apply empirical orthogonal function analysis to identify influential meteorological variables, and geographic regions where atmospheric measurements are most sensitive to anthropogenic mercury changes. We discuss how these insights can inform the mercury science-policy community on monitoring site location and metric selection.

WO-002

A DEVELOPMENT OF EMPIRICAL MODEL FOR MERCURY NET EXCHANGE FLUX BETWEEN AIR AND SOIL SURFACE

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Mercury (Hg) emissions from natural surfaces contribute a large portion of total Hg emissions in a global scale; however, there is a huge uncertainty on natural emissions inventory. According to UNEP, natural emissions and re-emissions can be categorized into five groups including biomass burning, soil surface, vegetation, geogenic, and oceans. Among these categories, Hg emissions from soil surfaces contribute about 30% of total Hg emissions. In this study, air-soil surface exchange flux of Hg was measured from various soil types including deciduous and coniferous forest floors, grassland, crop field, and lawn throughout a year using dynamic flux chamber (DFC) made of FEP (Fluorinated Ethylene Propylene) Teflon film. Tekran 2537B was used to detect the Hg concentrations inside and outside of DFC. Influencing factors for Hg exchange flux were investigated, and empirical equations estimating Hg flux were derived based on the measurements. In forest floor, different characteristics of Hg emission were observed for leaf-on (summer, autumn) and leaf-off period (spring). Volumetric water content in soil was the most important parameter during leaf-on period because solar radiation nearly reached on the surface due to the high leaf area index (LAI). On the other hand, the most important factors were UV and soil temperature for leaf-off period. In open fields, Hg emission was mainly controlled by soil temperature and UV irradiation for all period. Hg emission flux was also measured from hazardous waste landfill area, and it peaked about 3 h before solar radiation peaked, possibly because of reducible Hg being abundant at the soil surface. Four different models were empirically derived for Hg fluxes from deciduous and coniferous forest soils during leaf-on and leaf-off periods and from open field. In future, one governing equation which can depict Hg exchange flux from all kinds of soil surfaces will be developed, and hopefully presented at the conference.

WO-003

ATMOSPHERIC MERCURY TEMPORAL TRENDS IN THE NORTHEASTERN UNITED STATES FROM 1992 TO 2014: ARE MEASURED CONCENTRATIONS RESPONDING TO DECREASING REGIONAL EMISSIONS?

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Long term atmospheric mercury measurements at Underhill, VT (VT99) and Huntington Forest, NY (NY20) from 1992 to 2014 and 2005 to 2014, respectively, were used to determine concentration trends using the Mann-Kendalls tau test with Sens slope estimator. Data from these sites, generally downwind of large Hg sources in the Midwestern U.S., are the longest record of ambient Hg concentrations available in the U.S. At VT99 concentrations of gaseous element mercury (GEM), gaseous oxidized mercury (GOM) and particle bound mercury (PBM) declined with rates of -1.8%, -3.2% and -6.7% per year, respectively. At NY20 GEM and GOM concentrations declined with rates of -1.6% and -7.8% per year. However, PBM concentrations increased at a rate of 2.0% per year likely related to wood combustion. A trajectory ensemble analysis using potential source contribution function indicates the source locations associated with high mercury concentration changed from the Toronto-Buffalo and Pennsylvania areas to east-coast urban centers. The declining GEM concentrations in the Northeastern United States are positively correlated with decreasing SO2 emissions in the upwind area. Overall, the results indicate that decreased mercury concentrations measured during the past decade are consistent with decreased Hg emissions from regional point sources and that increasing global emissions have not overwhelmed those decreases.

WO-004

FIVE-YEAR RECORDS OF MERCURY CONCENTRATIONS OBSERVED AT GROUND-BASED MONITORING SITES IN THE FRAMEWORK OF THE GMOS GLOBAL NETWORK

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Long-term monitoring data of ambient mercury (Hg) on a global scale to assess its emission, transport, atmospheric chemistry, and deposition processes is vital to understanding the impact of Hg pollution on the environment. The Global Mercury Observation System (GMOS) started in November 2010 with the overall goal to develop a coordinated global observing system to monitor Hg on a global scale, including a large network of ground-based monitoring stations, ad hoc oceanographic cruises and measurement flights in the troposphere and lower stratosphere. To date, more than 40 ground-based monitoring sites constitute the global network covering many regions where little to no observational data were available before GMOS. This work presents atmospheric Hg concentrations recorded worldwide, analyzing Hg measurement results in terms of temporal trends, seasonality and comparability within the network. Major findings highlighted a clear gradient of atmospheric Hg concentrations between the Northern and Southern hemispheres, confirming that the gradient observed is mostly driven by local and regional sources, which can be anthropogenic, natural or a combination of both. In order to understand the atmospheric cycling and seasonal depositional characteristics of Hg, wet deposition samples were also collected at 17 selected GMOS monitoring sites providing new insight into baseline concentrations of THg concentrations in precipitation particularly in regions, such as the Southern Hemisphere and tropical areas where wet deposition were never investigated before, opening the way for additional measurements across the GMOS network and new findings in future modeling studies highlighting the need of integrated measurements in ambient air and rainwater samples to improve our understanding of deposition processes and oxidation mechanisms. These new observations in fact, give scientists and modelers some insight into baseline concentrations of Hg concentrations in air and precipitation with the overarching benefit which clearly consists in the advancement of knowledge about Hg processes on global scale.

1f: Quantifying mercury emissions from energy generation

WO-005

EMISSIONS AND ISOTOPE SIGNATURES OF HG FROM COAL-FIRED POWER PLANTS IN SOUTHERN CHINA

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Mercury (Hg) emitted from coal-fired power plants (CFPPs) is one of the most important anthropogenic sources. China is the largest coal consumer in the world, and CFPPs burned one half the coal used in China. During the past 10 years, Chinese CFPPs have sequentially installed the flue gas desulfurization (most limestone-gypsum) and DeNOx system (most SCR). Since FGD and DeNOx system have obviously synergetic effect on Hg removal, more work are needed to update the Hg emission factors. Hg isotope signatures from CFPPs are also important for source apportionment. Guizhou province in southwest China is rich in coal, and ranked No.1 in southern China. Coal in Guizhou feathered with high sulfur and ash content. In this research, we studied 14 CFPPs in Guizhou during 2014 to 2016, including 2 CFB (circulating fluidized bed) boilers and 12 PC (pulverized coal) boilers. Hg in the flue gas were sampled with Ontario Hydro Method (OHM) and detected with CVAAS (F732). Total Hg in solid samples such as coal, bottom ash, fly ash, flue gas filters, limestone and gypsums were determined with Lumex CVAAS. Hg isotope signatures in the flue gas and solid samples were detected with MC-ICP-MS (Nu Instruments, Nu plasma model II). Total Hg in the stack flue gas ranged from 0.14 to 3.92 $\mu g/m^3$, with CFB boiler emitted (average 0.21 $\mu g/m^3$, N=2) much lesser than PC boilers (average 1.17 $\mu g/m^3$, N=12). The total Hg removal efficiency for CFB boilers ranged from 98-99%, and 87-99% for PC boilers. Hg emission levels reduced dramatically for PC boiler than several years ago. Most Hg emitted from the CFPPs is in Hg^0 form. Hg concentration and speciation in the flue gas were determined by the coal property, boiler type and air pollution control devices. Mass-dependent fraction (MDF) was found between different coal combustion products, with lightest for the fly ash, and heaviest for the flue gas, with up to 6‰ difference in $\delta^{202}Hg$. MDF were also found between different Hg species in the flue gas, with Hgp the lightest, then Hg^{2+}, and Hg^0 the heaviest. Mass-independent fraction (MIF) was found in flue gas of some CFPPs, which may be caused by the catalytically oxidation of Hg^0 in SCR and H_2SO_4 production process during the organic amine desulfurization. Hence, Hg isotopic emissions from CFPPs can't be predicted by the feed coal.

WO-006

MERCURY AND PYRITIC SULFUR REDUCTION BY PREPARATION OF U.S. ILLINOIS BASIN COALS

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The Illinois Basin is the third largest producer of U.S. coal, after the Powder River Basin and the Appalachian Basin, respectively. Due to its proximity to U.S. coal-fired power generation and resulting low transportation costs, interest in high sulfur Illinois Basin coals has increased despite an overall decline in U.S coal production resulting from replacement by gas-fired power generation. Greater adoption of flue gas desulfurization in the U.S. fleet has made the high sulfur content of these coals less limiting. Nonetheless, Illinois Basin coals are commonly prepared prior to delivery to reduce mineral matter and improve heating value, with corresponding sulfur reduction. Mercury reduction occurs as a co-benefit of coal optimization for these other parameters.

As part of a larger investigation of the controls on mercury distribution in Illinois Basin coals, in the present study, mine mouth coal preparation circuits in in southern Illinois and southwestern Indiana were sampled to determine reduction of mercury and pyritic sulfur in these operations. In southern Illinois, the cleaning circuit processes Herrin (#6) coal, the most widely used coal in Illinois. Feed coal to this circuit contains 5.4% total sulfur, 4.5% pyritic sulfur, and 0.24 ppm Hg (as-received basis). The cleaned product, a combination of three cleaned size fractions, has a total sulfur content of 2.4%, pyritic sulfur of 0.9% and a Hg concentration of 0.09 ppm, which is below U.S. (0.11-0.12 ppm) and world (0.10 ppm) averages for mercury in delivered coal. Regression of pyritic sulfur vs. mercury for all eight samples from this circuit yields a positive correlation with an r2 of 0.89, supporting an association of Hg with pyrite as indicated in previous studies.

For Illinois Basin coal in Indiana, preparation circuit feed coals include the Springfield (#5), Bucktown (#5a), and Hymera (#6), coals, producing a composite product, and a separate preparation circuit for the Danville (#7) coal. For the Danville feed coal, having a total sulfur content of 1.7%, and a pyritic sulfur content of 0.8%, these values are reduced to 1.6% and 0.7%, respectively (as-received basis). In the composite circuit feed, pyritic sulfur ranges from 0.5% (Hymera coal) to 7.9% (Springfield coal), with a cleaned product pyritic sulfur of 1.9%. Determination of mercury in each Indiana circuit is in progress. In the absence of nationwide limits for mercury emissions from U.S coal-fired power generation, coal preparation remains an important means of reducing mercury emissions from coal use.

WO-007

EFFECTIVENESS OF MERCURY CONTROL STRATEGIES ON COAL-FIRED BOILERS IN THE US: A MATS REPORT CARD

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The Mercury and Air Toxics Standard (MATS) came into effect for almost all coal-fired power plants in the US on April 16, 2016. Power plants must now report their hourly mercury emissions to the US Environmental Protection Agency (EPA) on a quarterly basis. Plants in the US employ a variety of strategies to reduce mercury air emissions. The most common mercury control strategies are powdered activated carbon injection (ACI) and flue gas desulfurization (FGD) systems. The addition of halogen additives to the coal is sometimes used with both these technologies. In addition, ACI is sometimes used on boilers with FGD systems. The result is a myriad of different technology combinations in use for mercury control. Using information on the control technologies at specific plants as well as the reported Hg emissions, we assess the efficacy of different control strategies. This information will prove useful to countries that are considering wide-spread implementation of mercury control on coal-fired boilers.

WO-008

IMPACTS OF MERCURY EMISSION REDUCTIONS OF COAL-FIRED POWER PLANTS IN CHINA THROUGH IMPLEMENTATION OF THE MINAMATA CONVENTION ON MERCURY

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As one of the primary atmospheric point sources in the Minamata Convention on Mercury, coal-fired power plant bears the brunt of mitigation stress, especially for the relevant source which covers at least 75 percent of the emissions. In order to identify relevant source and obtain a deep insight of temporal and spatial characteristics of atmospheric mercury emissions from coal-fired power plants in China, a unit-based method is developed based on detailed information of unit capacity, electricity generation, coal consumption, air pollution control devices and geographical locations. The national total Hg emission in 2015 is estimated at 75 t, of which more than 60% is released from units with size lager than 300MW. The top three provincial emitters are Inner Mongolia, Jiangsu and Shandong, where power plants are densely concentrated. The average Hg-intensity is about 18.9 g/kWh in 2015. Based on the current mercury emission inventory, three scenarios of coal consumption and application of particulate matter/ sulfur dioxide/ nitrogen oxides/mercury (PM/SO2/NOx/Hg) control devices are projected to discuss in the time horizon from 2015 to 2030. Under the current coal consumption pattern and air pollution control policies without additional activated carbon injection (ACI), the mercury emissions would increase to 88 t in 2030. With the widespread application of fabric filter (FF) and application of ACI on 50% of Relevant Source, the mercury emission could reduce by 40% in 2030. Through the application of FF on 100% and ACI on 80% of relevant source, the mercury emission in 2030 can be decreased by 64% from the level of 2015. Considering these three scenarios, GEOS-Chem model is used for the evaluation of future mercury pollution levels.

2a-2: Sources and cycling of mercury in coastal ecosystems

WO-009

MERCURY METHYLATION AND DEMETHYLATION DYNAMICS AT AND NEAR THE SEDIMENT WATER INTERFACE OF CONTAMINATED ESTUARIES

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Sediments are a known sink for inorganic mercury (Hg) entering into coastal ecosystems, and they foster a geochemical environment conducive to high Hg methylation rates. Therefore, they have been considered a major source of methylmercury (MeHg) to estuarine water columns and coastal food webs. However, there is frequently no correlation between sediment and forage fish MeHg levels across coastal systems, suggesting the presence of a different, potentially more significant source of MeHg available to pelagic organisms. Of particular interest is the potential for net water column MeHg production relative to sediment production and flux to the water column, especially within flocculated material suspended and/or at the sediment water interface. While most studies focus on methylation within an integrated sediment section (typically, the top 2 or 4 cm), it is possible that methylation rates are higher in flocculated, unconsolidated surface sediment than in the deeper sediments; this material is also more likely to re-enter the water column via resuspension where it may be more relevant for biotic exposure. To better understand the importance of in situ methylation and exchange processes between estuarine sediments and the overlying water column, we measured methylation and demethylation potentials in estuaries of varying historic mercury contamination using isotopically labeled mercury species (Me199Hg and 200Hg(II)). Four geochemically diverse zones were investigated in 2016; surface water, bottom water, unconsolidated surface sediments, and consolidated near-surface sediments. Water samples were incubated unfiltered in the dark and in the light. Abiotic demethylation was monitored with 0.2 µm filtered water samples kept in the light. Results suggest that methylation within the water column is complex and more highly variable in space and time within estuarine systems than net MeHg production in the sediment. Our initial estimates suggest that integrated water column methylation is comparable to the potential MeHg flux from the sediments at certain locations within an estuary. Overall, it appears that the surface floc layers in the systems studied in 2016 have dissimilar methylation and demethylation rates to deeper, consolidated sediments, with slightly higher rates in the unconsolidated floc layer. The results of the 2016 studies will be discussed in detail and will be contrasted to a similar study we conducted in 2015 from a broader range of sites along the US East Coast. Our overall findings suggest that water column methylation in coastal ecosystems should not be ignored when considering sources of MeHg to coastal food webs.

WO-010

PARTICULATE METHYLMERCURY DYNAMICS IN ESTUARINE WATER COLUMNS OF VARYING HISTORIC MERCURY CONTAMINATION

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Water column methylmercury (MeHg) concentrations are an important indicator for food web mercury burdens in coastal aquatic ecosystems. Several studies have observed strong correlations between forage fish MeHg body burdens and water column particulate MeHg, but less of a relationship to sediments where high rates of mercury (Hg) methylation are frequently measured. To further study this, we compared water column methyl- and total Hg dynamics along estuarine salinity gradients in systems of varying historic mercury contamination including Berrys Creek and the Hackensack River in New Jersey, the Penobscot River in Maine, and the Pawcatuck River in Connecticut/ Rhode Island. Each system was sampled twice in 2016, once in late spring and once in mid-summer, with some sites also sampled several times over a tidal cycle. To better refine our understanding of particulate methylmercury dynamics, the suspended particles were sampled in bulk and as a 20-0.45 µm size fraction using sequential filtration techniques. Auxiliary data collected to help explain the particulate trends include chlorophyll a and phaeopigments, suspended solids, carbon/nitrogen/ sulfur concentrations and isotopic signatures, and dissolved methyl- and total Hg. Sediments were also collected at the time of sampling to assess background mercury contamination. Our results indicate that MeHg and total Hg are overall greater at the more contaminated sites. However, the water column particulate pools do not directly reflect the near surface sediment concentrations at the location in which they were collected, particularly for MeHg, suggesting that the suspended pool of MeHg in the water column may not be directly related to sediment production. Dissolved MeHg dynamics track the particulate MeHg in the water column. However, in the more contaminated sites the majority of the water column MeHg is associated with particles in comparison to more pristine sites where a greater portion of the MeHg is in the dissolved phase. We will discuss the implications of our results in terms of understanding the mechanisms of MeHg transfer to the food web, and its variability across coastal ecosystems.

WO-011

QUANTIFYING STABLE ISOTOPE TROPHIC TRANSFER OF INORGANIC MERCURY AND METHYLMERCURY FROM DIATOMS TO THE COPEPOD ACARTIA TONSA AND FIELD ZOOPLANKTON

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Methylmercury (MeHg) exposure is a recognized health concern, as it can cause brain and neurological damage in humans and animals. In marine food chains MeHg is first bioconcentrated in phytoplankton, then transferred up the food chain through consumption by herbivorous zooplankton, planktivorous fish, and eventually larger predators. However, there is relatively little experimental data on mercury (Hg) and MeHg in primary producers (phytoplankton) and primary consumers (zooplankton). There have been few measurements of the uptake and assimilation efficiencies (AE) for plankton at environmentally relevant levels of exposure, or that have been undertaken using native field populations, even though these assemblages represent the base of the marine food chain, and the initiation of MeHg exposure for higher trophic levels. The current study was therefore aimed at understanding the dynamics of Hg and MeHg uptake and trophic transfer at the lower trophic levels.

Feeding experiments were performed using stable isotopes of inorganic Hg (200Hg) and MeHg (CH3199Hg) in order to determine AEs for the specific Hg species, as well as to demonstrate potential effects of concentration and size of algae on their accumulation of Hg and MeHg as well as the bioaccumulation into the copepod Acartia tonsa. The average AE for ^{200}Hg from copepods feeding on the smaller diatom (*Thalassiosira pseudononna*) was 41 +/- 15 % and 32 +/- 17 % for the larger diatom (*Thalassiosira weisflogii*). The AEs were greater for $\mathrm{CH}_3^{199}\mathrm{Hg}$, ranging around 71 +/- 9 % for the smaller diatom and 88 +/- 4 % for the larger diatom.

Assimilation Efficiencies were higher for Hg than reported for previous studies, suggesting that AEs may be related to exposure concentration. Stable isotope feeding experiments were additionally performed for algae species fed to size-fractioned field populations of zooplankton collected from different locations in Long Island Sound, and yielded varying results depending on the season of collection. Our results provide evidence that Hg and MeHg assimilation differs with zooplankton size and species composition. Overall, these experiments demonstrated that there was significant relationship between Hg and MeHg exposure concentration and algal uptake and trophic transfer to zooplankton. Furthermore, these experiments also provided evidence for earlier suggestions of active uptake of MeHg into algae at low (pM) concentrations. These differences in uptake and AE could impact modeling of the transfer of MeHg within ocean food chains, and therefore predictions of the impact of changing emissions on ocean fish concentrations.

WO-012

TOTAL MERCURY AND MONOMETHYLMERCURY IN MARINE STRATUS CLOUD WATER AS SAMPLED BY AIRCRAFT OVER THE PACIFIC OCEAN ALONG THE COAST OF CALIFORNIA, SUMMER 2016

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The Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter aircraft was used to sample cloud water with a Mohnen slotted-rod cloud water collector during 16 flights in July and August of 2016 off the coast of central California. Total mercury (HgT) and monomethylmercury (MMHg) were quantified in cloud water samples and relationships were observed with ancillary measurements of cloud physical and chemical parameters. Mean (± 1s) concentrations of HgT and MMHg from all samples were 9.17 ± 5.95 (N = 99) and 0.87 ± 0.66 ng L-1 (N = 19), respectively. The 19 composite samples that were analyzed for MMHg had a mean %MMHg compared to HgT of 9.5%, a value that is significantly higher than %MMHg found in California coastal rain water (~2%), but nearly equivalent to the %MMHg value found in California coastal fog water (~7%). Correlations with ancillary parameters suggest that major sources for both HgT and MMHg in cloud water were from the sea surface, especially over areas of strong wind-driven upwelling. Two flights in particular, that sampled between Monterey Bay in the south and Bodega Bay in the north, passed over mesoscale upwelling eddies as indicated by satellite altimetry, and produced samples with the highest HgT and MMHg concentrations (25.2 and 2.9 ng L-1, respectively). The samples from these flights revealed significant negative correlations of HgT and MMHg with the meridional component of wind speed (v), indicating a relationship with wind-driven upwelling. The samples from these flights also revealed significant negative correlations of HgT and MMHg with sea surface temperature and aircraft altitude, and significant positive correlations with the sodium ion (tracer of sea spray). These findings are consistent with our oceanographic measurements of dimethylmercury (DMHg) and dissolved gaseous elemental Hg (DGM) in this same region, which were found to be supersaturated in surface waters where mesoscale upwelling eddies were present, resulting in a sea-air flux of these relatively insoluble species.

2I: Safe and reliable handling of mercury in science & technology

WO-013

SCALE-UP EFFECT ON SULFIDE PROCESSING OF WASTE ELEMENTAL MERCURY USING A PLANETARY BALL MILL

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The Minamata Convention on Mercury was adopted in 2013, which requires that elemental mercury collected from mercury waste should be managed under safe conditions. Elemental mercury is liquid at room temperature and has a high volatility, allowing it to move easily in the environment. It is preferable that elemental mercury be recovered by a distillation method that converts it to a more stable chemical form for long-term storage or permanent disposal. We have developed a stabilization method by producing mercury sulfide using a planetary ball mill. However, in order to apply the method to a real plant, the challenges on the scale-up effect should be confirmed. In this study, we conducted scale-up tests to confirm that mercury sulfide can be effectively produced using a larger sized planetary ball mill, and investigated options for improving the operating conditions for stabilizing mercury. Firstly, the mercury concentration in the headspace above the stabilized materials was measured to evaluate degree of the reaction between elemental mercury and sulfur.

In previous studies, the maximum capacity for sulfide processing was calculated as 120 g-Hg/h/pot using 250 mL pots with balls of 19.04 mm diameter in a laboratory-scale planetary mill. In this study using 2,400 mL pots with balls of 19.04 mm diameter, the maximum capacity (1152 g-Hg/h/pot) was equivalent to the value calculated by extrapolating the results from previous laboratory-scale experiments. Ball size was the most important parameter studied under various conditions. As the ball diameter increased, the stabilization progressed faster under stronger pulverization. When the ball diameter was 25 mm, the reaction time was shortened to 20 min. The powdered products obtained using the planetary mill were identified by X-ray diffraction analysis of cinnabar and metacinnaber, two types of mercury sulfide. Our study demonstrates that sulfide processing of mercury can be effectively conducted using a larger sized planetary ball mill.

WO-014

THE ROLE OF MERCURY IN NUCLEAR FUSION TECHNOLOGY

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Nuclear fusion, the merging of two hydrogen isotopes (deuterium and tritium) to helium under the release of huge amounts of energy, is considered as one important element to satisfy the world-wide growing demand of energy. This technology would be carbon-free, safe, almost unlimited in resources and does not produce long-living radioactive waste. In several countries in the world (EU, USA, Japan, China, Korea, India, Russia) large development programs have been launched to bring this technology to maturity. To realize fusion power plants, high technical challenges have to be tackled. Two of them are closely linked to the use of mercury.

One area of specific concern is the fusion fuel cycle which processes large amounts of the radioactive tritium fuel. Tritium is a weak -emitter and decays with a half-life of 12.3 years to form helium. As the tritium isotope is chemically reactive and easily implanted in any organic species via an isotope exchange reaction against the normal hydrogen, all such hydrogen-containing species (such as polymers, organic working fluids, oils, lubricants, hydrocarbons etc) are not allowed to be used in the processing machines. The best fully tritium-compatible alternative working fluid is mercury, as it does practically not interact with tritium.

As tritium itself is not a natural resource, it is produced in-situ via a nuclear reaction with lithium-6 that takes place in the so-called tritium breeding blankets attached to the first wall of the reactor. The lithium-6 has to be taken from natural lithium which is a lithium-6/lithium-7 mixture with 7.5% lithium-6. There are various technologies to enrich the lithium-6 content of natural lithium to the required level; the most promising approach is based on isotope exchange between lithium salt and lithium amalgam, exploiting the very high affinity of mercury to lithium-6.

This paper shortly presents the EU roadmap to a fusion power plant until the 2050s. It then introduces in the main missions and delineates the technical requirements for the fuel cycle and the breeding blankets. Here, issues of safe and reliable mercury handling with minimum releases are addressed. Finally, an optioneering exercise is conducted that clearly supports the use of mercury related technologies, and a near- and mid-term RD programme is outlined to bring these concepts to higher technical readiness levels. This paper is also thought to create awareness of these opportunities in the industrial mercury community.

WO-015

MERCURY AS WORKING FLUID IN SPECIAL-PURPOSE VACUUM PUMPS

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Since the very early days of vacuum technology, mercury is used in various applications: For the measurement of pressure, Evangelista Torricelli used a glass tube filled with mercury in 1643. The first high vacuum pump on the market, invented by Wolfgang Gaede in 1915, has been operated with mercury as working fluid and opened the door to scientific fields like accelerator physics and space applications that are unthinkable without high vacuum conditions.

Nowadays, the importance of mercury in vacuum technology has decreased: pressures are now measured using electronic gauges and for vacuum pumping, pumps are available on the market that are dry (i.e. no working fluid needed) and simple to operate (i.e. no heat-up times, no cool water and cold traps required). However, despite of all this new technologies, there is still a small but growing field where mercury as working fluid cannot be replaced: high vacuum pumping for very reactive and radioactive gases.

In the past, mid of the 20th century, mercury has been used extensively for vacuum pumping and tritium (a radioactive hydrogen isotope) processing. At that time, mercury was not handled with care and a lot of environmental contamination occurred, leading to a bad image of this element. In the 21st century, the development of a new source of energy is ongoing that needs a very large vacuum system where huge amounts of tritium have to be processed: nuclear fusion.

This paper presents the development of novel vacuum pumps for fusion applications at KIT, namely mercury ring pumps and linear mercury diffusion pumps. For both pump types, the requirements are defined and the development path is shown up. Special focus during the development is given to the minimization of the working fluid inventory and the trapping of mercury inside the pumps. As conclusion, future RD activities are outlined.

4b: Contaminated site assessment and management: Lessons for technical assistance under the Minamata Convention

WO-017

BEST MANAGEMENT PRACTICES FOR MITIGATING AQUATIC SEDIMENTS CONTAMINATED WITH MERCURY - LESSONS FROM THREE CASE STUDIES

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Under the Minamata Convention (Articles 9 and 12) countries are encouraged to identify, assess, and remediate sited contaminated with mercury (Hg) in order to reduce the risks to humans and biota. However, there is an increasing concern over the potential for full recovery of lake and reservoir ecosystems, many of which have experienced a legacy of Hg contamination. While the cessation of the direct source may result in decreases of Hg concentrations in water and biota, the long-term recovery of the ecosystems is not always achieved.

Using three case studies of Hg-contaminated lakes (Calero Reservoir in California, USA, Lake Pena Blanca in Arizona, USA, and Onondaga Lake in New York, USA), this work illustrates current practices for mitigating Hg contamination in lake sediments. The three lakes experience seasonal anoxia in the hypolimnion and substantial build-up of methylmercury (MeHg). Calero Reservoir is located in the New Almaden mining district, one of the largest sources of mercury in North America. Elevated total Hg and MeHg concentration were observed in sediment, water, and biota. Engineered oxygen addition to bottom waters, using pure oxygen gas, was chosen as remedial alternative. Lake Pena Blanca receives runoff from Hg tailings of abandoned gold mines located within its watershed. Removal of the Hg source and complete excavation of the lake sediments was undertaken. New, clean sediments were placed, the lake was naturally refilled with water, and fish was restocked in the lake. Onondaga Lake received ionic Hg inputs from the waste stream of a chlor-alkali plant that operated on the shores of the lake. Elevated

Hg concentrations were reported in the water column and pelagic fish. Whole-lake nitrate addition to the hypolimnion of the lake was the preferred remedial alternative.

The author compares and contrast the effectiveness of the three remediation techniques and provides recommendations for the selection of proper, cost-effective, and environmentally-sound remediation based on site-specific conditions and regulatory goals.

WO-018

EVALUATION OF PHYTOREMEDIATION TECHNOLOGIES FOR MERCURY-CONTAMINATED SITES BY ADAPTING THE SOURCE-TO-OUTCOME FRAMEWORK

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The Minamata Convention on Mercury was created to protect human health and the environment from the anthropogenic emissions and releases of mercury compounds by curbing and/or controlling the different life-cycle stages of mercury, including the management of contaminated sites. Phytoremediation, a group of technologies that reduce, remove, degrade or immobilize environmental toxics that are primarily of anthropogenic origin, is considered to be a cost-effective, safe and environment-friendly technology to clean-up contaminated sites. While phytoremediation is a promising technology, its application in mercury-contaminated sites is poorly understood, thus uncertainties remain as to its application. Here, we develop a framework for evaluating phytoremediation technologies for mercury-contaminated sites using the source-to-outcome based approach. A review of published works on mercury phytoremediation was done and the identification of the key environmental decision-making criteria is guided by the core/non-core model for sustainable remediation of contaminated sites. The existing phytoremediation technologies for mercury revealed that potential wider environmental impacts may result from the various inputs of substances and organisms by the remediation work. These include movement of mercury to groundwater resources through chelating agents, threats to biodiversity and ecosystem structure and function of non-native and transgenic species, and production of contaminated plant materials that need environmentally-sound disposal, among others. The source-to-outcome framework developed specifically for mercury-contaminated sites is important in understanding and visualizing the specificity of both the problem caused by mercury and the phytoremediation process and their relationship in the feedback mechanism. We propose that to further expound on the work, one should include the identification of core/non-core socio-economic factors that can be undertaken to provide a more holistic view of the decision-making process by ensuring that the analyses are grounded on the principles of sustainable development.

WO-019

THE SCREEN OF LOW-HG CROPS AT MERCURY MINING SITE IN CHINA: IMPLICATION FOR BUILDING AN AGRICULTURAL SCHEME FOR SAFETY CROPS PRODUCTIONS

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In China, the majority of mercury mines locate at Karst region in the southwest of China, especially in Guizhou province. The Karst region is characterized as the vulnerable and scarcity of farmland, the farmer depend on farmland as the main revenue resource. Soil surrounding Hg mining areas is heavily contaminated with mercury and thus causing the contamination of crops with mercury. The inhabitants living at Hg mining areas were exposed to mercury by consumption of Hg-contaminated crops. Therefore, the establishment of theme for safety crop production at mercury mining area is necessary for maintaining the eco-safety at mercury mining area.

Although many remediation methods have been developed, no one can be used in such a large scale. The three mercury mines including YunChangPing mercury mine, Wanshan mercury mine and Wuchuan mercury mine, which are located in Guizhou province, were chosen as our study areas. In order to screen the crops which are characterized as low accumulation of Hg, the distribution of Hg in air, calcine, soil and crops at mercury mining area were investigated. We proposed a safety agricultural regulation scheme which can largely ensure the original agricultural use of farmland and the original benefits of farmers based on growing the crops which are characterized as low accumulation of Hg and the database of local land use. By using the protocol of environmental economy, we calculated the potential benefits of agricultural products raised by the use of proposed agricultural regulation scheme and quantify the extent of decrease of human exposure to Hg.

In comparison to previous studies, the concentration of Hg in atmosphere and surface water showed a trend of decrease, but the values were still greatly exceeded those at background sites. No obvious change of mercury concentration in soil was observed. The total mercury concentration in the edible parts of different crops is significantly different from each other. The Hg concentration in the edible part of turnip (corresponding rhizosphere soil mercury content <10 mgkg-1), watermelon (corresponding rhizosphere soil mercury content <50 mgkg-1), strawberry and corn (corresponding rhizosphere soil mercury content <100 mgkg-1), and potato (corresponding rhizosphere soil mercury content <250 mgkg-1) are lower than the national food quality standard (GB2762-2012), and thus belonging to low Hg accumulation crops. By changing agriculture practices, we can significantly reduce mercury exposure in local inhabitants in mercury mining areas in Guizhou, China.

WO-020

DEVELOPMENT OF ANALYTICAL METHOD FOR SEPARATION AND QUANTIFICATION OF METHYL/ ETHYLMERCURY IN RADIOACTIVE TANK WASTE

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Savannah River Site (SRS) is a nuclear reservation owned by the U.S. Department of Energy that was used during the Cold War to refine nuclear materials for deployment in nuclear weapons. In fulfilment of the mission and vision of SRS, the legacy waste generated on-site is treated in a way that protects public health and the environment. Treatment of legacy waste at SRS includes vitrification into borosilicate glass and storage in stainless steel canisters. In addition to its environmental and public health impact, mercury, which is present at high concentrations due to its use as a catalyst in the dissolution of uranium-aluminum alloy fuel rods, can be corrosive to the off-gas equipment used in the vitrification process. Therefore, a method has been developed to speciate organic mercury in high-activity samples of radioactive tank waste to assure compliance with SRS Waste Acceptance Criteria. This quantitative method was developed and optimized for various derivatizing agents and automated purge and trap (PT), gas chromatography (GC), and atomic fluorescence spectroscopy (AFS) to be performed without sample distillation. Two derivatizing agents were evaluated, tetraethylborate and tetrapropylborate, to allow separate work to be performed on the samples for ethylmercury speciation. Total method runtime was significantly reduced, from 5.33 workhours per sample to 0.60 workhours per sample, by the removal of distillation. Due to the unique characteristics of this work, analyst-time, consumables, and waste generation were also optimized to prevent excessive radiation exposure. This method has produced quantitative results from simulated tank samples with a mean accuracy of 89.6% and mean precision of 4.61% RSD. Derivatization by propylation did not produce significantly different quantitative results for methylmercury ($p>0.05$), while permitting the quantification of ethylmercury. Direct analysis of samples, without distillation, improved mean accuracy by 11.4% ($p=0.00172$). This method was compared with other industry accepted methods of methylmercury and ethylmercury analysis, including inductively coupled plasma mass spectrometry, and atomic absorption spectroscopy, and was found to produce statistically similar quantitative results ($p>0.05$). Due to the highly accurate and precise quantification, fast method runtime, compact nature of the instrumentation, and the absence of excessive sample preparation, this method was determined to be ideal for the highly unique and hazardous nuclear waste tank samples analyzed at Savannah River Site and Savannah River National Laboratory. Future research will explore assimilating this method with inorganic mercury speciation using thermal desorption/AFS.

4d-1: Technologies and approaches for mitigating mercury emissions

WO-021

NANOSELENIUM SPONGE TECHNOLOGY FOR MERCURY REMOVAL FROM WATER

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Mercury represents a serious and persistent threat to public health due to its persistence and bioamplification throughout the food chain. Numerous methods, notably the use of activated carbon sorbents, have been employed to remove mercury from water. Current limitations include the inability to remove mercury below 10 part per trillion (ppt), need of water pretreatment systems, and reversible interactions with mercury, which could represent a secondary pollution. There is an urgent need for rapid technologies that can remove mercury from water below its environmental levels in a cost-effective fashion. In this work, a store-bought polyurethane sponge was used as a 3D matrix to grow selenium nanomaterials (NanoSe) on the surface and throughout the bulk of the sponge fibers (International Patent Application # PCT/US2016/056850). The NanoSe sponge was shown to remove mercury to levels that are undetectable by state of the art analytical methods (detection limit < 0.2 p.p.t) in less than 5 seconds. Furthermore, the sponge does not capture water nutrients, removes other heavy metal pollutants, and shows no cytotoxic effect on human cells, while exhibiting strong antimicrobial properties that prevent biofouling. Finally, the high affinity of Hg for Se results in irreversible sequestration and detoxification of mercury by the sponge, allowing the NanoSe sponge to meet the US-EPA requirements for leachability and landfill disposal.

WO-022

THE IMPORTANCE OF MODIFICATION OF ACID SITES FOR HG0 ADSORPTION/ OXIDATION IN THE PRESENCE OF NH3 OVER METAL OXIDES CATALYSTS

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Catalytic oxidation of Hg0 to Hg2+ by upstream SCR catalyst and removed by downstream air pollution control devices (APCDs) was supposed as an effective way to eliminate Hg0 emissions. The Hg0 oxidation efficiency was affected by many components in flue gas. In the presence of NH3, Hg0 oxidation was inhibited significantly over most of catalysts. It was believed that competitive adsorption of Hg0 and NH3 on the catalyst surface was the main reason for inhibition effect. Although plenty of catalysts, such as CeO2/TiO2, Fe2O3/TiO2, MnOx-CeO2/TiO2 and V2O5-WO3/TiO2, had been investigated for Hg0 oxidation, the mechanism of effect of NH3 on adsorption of Hg0 had been hardly reported. In this work, the competitive adsorption of Hg0 and NH3 on different catalysts was investigated to explore excellent catalyst for Hg0 oxidation in the presence of NH3. A novel reaction mechanism based on the modification of surface acidity was proposed to develop industrial catalyst for Hg0 oxidation.

The CuO/TiO2, CeO2/TiO2, Fe2O3/TiO2 and V2O5-WO3/TiO2 catalysts were prepared by ultrasonic assisted impregnation method. The XRD result indicated that CuO, CeO2, Fe2O3 and V2O5 was well-dispersed on the surface of TiO2. The adsorption performance of Hg0 was investigated in the absence/ presence of 100ppm NH3. The Hg0-TPD results indicated that the CuO/TiO2 catalyst showed the best Hg0 adsorption capacity, followed by V2O5-WO3/TiO2, CeO2/TiO2 and Fe2O3/TiO2 catalysts. In addition, the peaks of Hg0-TPD of all catalysts were mainly attributed to weak adsorption. In the presence of NH3, the adsorption performance of Hg0 was inhibited over all of the catalysts. However, CuO/TiO2 catalyst exhibited a superior performance on Hg0 adsorption compared to other catalysts. CuO/TiO2 catalyst showed the smallest BET surface area of 33.59 m2/g. XPS results displayed that the ratio of chemisorbed oxygen on CuO/TiO2 had no obvious difference compared with other catalysts. NH3-TPD spectra indicated that abundant weak acid sites appeared on CuO/TiO2 catalyst, while weak and medium-strong acid sites co-existedon V2O5-WO3/TiO2 catalysts. The weak acid sites strength per specific surface area were 983mol/m2 and 477mol/m2 over CuO/TiO2 and V2O5-WO3/TiO2 catalysts. The competitive adsorption of Hg0 and NH3 was mainly existed in the weak acid sites. It indicated that the appearance of abundant weak acid sites of CuO/TiO2 catalyst improved the adsorption performance of Hg0 in the presence of NH3. Modification of surface acidity is an effective way to develop excellent Hg0 adsorption/ oxidation materials in the presence of NH3.

WO-023

STABILIZATION OF MERCURY AS HGS WITH A WET CHEMICAL PROCESS

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The global evolution of environmental legislation (e.g. Minamata Convention on Mercury) creates a demand for a safe disposal of metallic mercury. Especially the chlor alkali industry that is currently switching its mercury based plants to mercury free technologies and is therefore looking for disposal solutions, but also the mining industry as well as the oil gas industry. The transformation of mercury a hazardous and toxic substance for both humans and the environment into mercury sulphide (HgS, cinnabar) before sending it to designated landfill sites is considered to be the safest way to dispose mercury. Mercury sulphide is not only the most stable and insoluble mercury compound but also non-toxic, it is therefore the most obvious solution to transform mercury, which is no longer needed or considered to be a waste, into this compound before it is disposed of.

The presented wet chemical process to transform mercury into mercury sulphide sets new milestones in terms of safety, conversion rate and process efficiency. The process employs a stabilisation reagent, which is mixed with pure liquid mercury. Active sulphur within the stabilisation mixture reacts with the metallic mercury to form HgS (cinnabar), resulting in a mercury-sulphide cake with less than 5 % water. A conversion rate of 99.999% of the mercury to mercury-sulphide is guaranteed. Since the process is a wet process it is not prone to gaseous mercury emissions, improving operational safety. The process has been operational since 2016 and has a capacity of approx. 1.000 t/year.

Taking into account the sensitive issues surrounding the safe disposal of mercury, traceability is a key requirement for the whole process of mercury stabilization. The complete traceability chain that has beenimplemented aroundthe stabilization process including external inspections, sampling, analysis and mass balancing is introduced and shown on practical examples.

WO-024

IMPACT OF ACTIVATED CARBON RAW MATERIAL SURFACE CHEMISTRY ON MERCURY REMOVAL FROM FLUIDS

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Activated Carbon is extremely effective and feasible at removing unwanted contaminants that may pose health threats such as mercury and it has been widely accepted for the removal of mercury (Hg) from coal-fired power plant flue gas and industrial effluent. Activated carbons surface chemistry can play a key role when removing Hg, therefore the characterization of activated carbons surface is essential to understand help simplify and better recognize the chemical reactions occurring on the surface of the activated carbon. This work examines the relationship between Hg removal and the concentration of the various types of oxygen functional groups on the surface of commercially available activated carbons synthesized from various raw materials. It will primarily study the enhancement of the carboxylic, lactonic and phenolic oxygen functional groups through post activation treatments on activated carbons exhibiting lignocellulosic and graphitic structures. Traditionally Boehm titrations have been used to determine these three acidic functional groups on the activated carbon surface based on the concept of acid-base neutralization analysis. This qualitative and quantitative technique has been extensively used on activated carbons of different origins to investigate and detect surface oxygen functional groups. In this work activated carbons were acid treated at varying concentrations which were then characterized for physical and chemical properties. The physical characterizations included surface area, pore volume, average pore size, and density. The chemical characterization techniques implemented to study the amphoteric nature of activated carbon were Boehm titrations and Fourier Transform Infrared (FTIR) Spectroscopy. Activated carbons with different concentrations of functional groups were compared for Hg adsorption and treated activated carbons showed greater removal than the virgin activated carbon. Carboxylic functional group concentration was associated with Hg uptake contradictory to other theories that suggest that an active site where electron sharing occurs is responsible for the oxidation and adsorption mechanisms of Hg.

1b: Biogeochemical cycling of mercury in the ocean

WO-025

FACTORS CONTROLLING THE PHOTOCHEMICAL DEGRADATION OF METHYLMERCURY IN COASTAL AND OCEANIC WATERS

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Many studies have recognized abiotic photochemical degradation as an important sink of methylmercury (MeHg) in sunlight surface waters, but the rate-controlling factors remain poorly understood. The overall objective of this study was to improve our understanding of the relative importance of photochemical reactions in the degradation of MeHg across a variety of marine ecosystems by extending the range of water types studied. Experiments were conducted using surface water collected from coastal sites in Delaware, New Jersey, Connecticut, and Maine, as well as offshore sites on the New England continental shelf break, the equatorial Pacific, and the Arctic Ocean. Filtered water was amended with additional MeHg at environmentally relevant concentrations, which was allowed to equilibrate with natural ligands before being exposed to natural sunlight. Water quality parameters salinity, dissolved organic carbon, and nitrate were measured, and specific UV absorbance was calculated as a proxy for dissolved aromatic carbon content. Degradation rate constants were very similar (0.87-1.67 1/day) across all water types tested despite varying characteristics, and did not correlate with initial MeHg concentrations or other environmental parameters. The rate constants in terms of cumulative photon flux were comparable to, but at the high end of, the range of values reported in other studies. Further experiments observed little effect of nitrate, chloride, and bromide on the reaction. The HydroLight radiative transfer model was used to compute solar irradiance with depth in three hypothetical water bodies coastal wetland, estuary, and open ocean allowing for the determination of water column integrated rates. Methylmercury loss per year due to photodegradation was also modeled across a range of latitudes from the Arctic to the Equator in the three model water types. Despite the low concentrations found in the surface mixed layer of the open ocean, the loss of MeHg was greatest due to increased penetration of all wavelengths, especially the ultraviolet portion of the spectrum which has a greater ability to degrade MeHg. Overall, this study helps to better constrain the degree to which photochemical degradation impacts the cycling of MeHg in surface waters and its transport from coastal waters to the open ocean.

WO-026

ELEMENTAL MERCURY PRODUCTION IN SEAWATER BY COASTAL BACTERIAL ASSEMBLAGES

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Elemental mercury (Hg0) evasion from surface seawater plays a principal role in the marine mercury cycle. Hg0 production in seawater is mainly controlled by abiotic (photochemical) and biotic (microbial) processes. In this study, we established a method using the gamma-emitting radionuclide Hg-203 as a tracer to evaluate the transformation of Hg2+ and methylmercury (MeHg) to Hg0 in seawater by coastal bacterial assemblages. The method, which used traps containing gold-coated beads to capture Hg0 released into air from seawater, can provide rapid and reliable Hg0 measurements that avoid potential contamination. Several natural bacterial assemblages in surface seawater collected 8 km off Southampton, New York, were used in our experiments. These bacterioplankton were contained in seawater collected 6 years prior to our study and stored in the dark at 4°C. Remarkably, these bacteria were still able to rapidly produce Hg0 following picomolar additions of 203Hg2+ or Me203Hg when brought up to 23°C in 2 days. Our results show that Hg0 production rates were independent of dissolved Hg2+ and MeHg concentrations, and were directly a function of bacterioplankton densities. Addition of antibiotics reduced Hg0 evasion to undetectable levels. These Hg evasion experiments showed that for 1 μm-filtered Long Island coastal waters from the Atlantic with natural bacterial assemblages and bacterial densities of about 1 x 106 ml-1, approximately 25% of Hg2+ and 18% of MeHg were transformed to Hg0 in 4 days at ~23°C. In Long Island Sound waters, with 5 x 106 bacterial cells ml-1, 60% of Hg2+ and 19% of MeHg were converted to Hg0 and trapped in the air within 4 days. When bacterial assemblages were exposed to Hg2+, the Hg0 production rate declined after one day, but the rate of Hg0 evasion from bacterial assemblages exposed to MeHg remained constant over 4 days, suggesting two distinct production pathways. Total Hg0 production for both Hg2+ and MeHg exposures at ~23°C were 6 times those at 4°C, indicating such transformations were mainly driven by metabolic processes.

WO-027

DISTRIBUTION OF MERCURY SPECIES IN THE WESTERN ARCTIC OCEAN

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Mercury (Hg) concentrations in Arctic wildlife and humans have increased during the Anthropocene at rates faster than those observed at temperate and tropical latitudes. One potential explanation for the anomalous increase of monomethylmercury (MMHg) in Arctic biota is that, superimposed on increasing atmospheric Hg deposition, climate change has exacerbated production and cycling of MMHg in the polar ocean. To better understand the distribution and cycling of Hg in the western Arctic Ocean, we measured dimethyl-Hg, monomethyl-Hg, and elemental and total Hg as part of the U.S. GEOTRACES Arctic cruise (GN01) in 2015 to the Bering Sea and Makarov and Canada Basins. Although Hg concentrations in the two basins were low relative to the Atlantic and Pacific Oceans, higher total Hg concentrations were observed in Arctic seawater that recently interacted with continental margins. Surface waters under ice contained elevated concentrations of total Hg and elemental Hg relative to ice-free surface waters. From our measurements, we are able to better understand sources, sinks, and cycling of Hg in the Arctic Ocean, and estimate that the Arctic Ocean receives about 20 kmol/yr of Hg from the Bering Strait, which is much less than the estimated atmospheric input (~400 kmol/yr). This comparison suggests that the atmosphere is the main source of Hg to the surface Arctic Ocean when compared to the Bering Strait, and we would expect concentrations in surface seawater and biota to respond to changes in atmospheric deposition.

WO-028

MERCURY IN THE MARINE WATERS OF THE CANADIAN ARCTIC

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Mercury (Hg) is a contaminant of major concern in the Arctic marine ecosystem for its high toxicity and biomagnification in the food web. In upper trophic level species, Hg concentrations are sufficiently high to pose heath risks to both animals and the Northern people who consume these animals as part of traditional diet. The dominant form of Hg that is transferred within the food web is monomethylmercury (MMHg), which is built up from their prey and ultimately from seawater. Although sedimentary production and release of MMHg can occur, recent studies indicate that the primary source of MMHg to seawater is in situ conversion of inorganic Hg(II) to MMHg in the water column. We have recently reported enriched methylmercury (MeHg, sum of MMHg and dimethylmercury) in subsurface seawater of the Beaufort Sea, and linked this subsurface peak to local and recent organic matter (OM) remineralization on the basis that MeHg has a short lifetime in seawater. Here we report depth profiles of total Hg (HgT) and MeHg from the ArcticNet/GEOTRACES 2015 cruise. In the Canada Basin (CB) and Baffin Bay (BB), HgT shows a transient-type distribution, with elevated concentrations in the surface and deep waters, and lower concentrations in the upper and middle ocean. Whereas in the shallower Canadian Arctic Archipelago (CAA), HgT concentrations are more uniform with depth, probably due to the enhanced terrestrial Hg input by river runoff and coastal erosion. Methylmercury in the Canadian Arctic exhibits surface minimum and subsurface peaks, similar to those observed in the Beaufort Sea and other world oceans. Positive correlations between MeHg and phosphate concentrations evidence the association of MeHg production in seawater with OM remineralization. Though with lower HgT and productivity than BB, MeHg in CB and West CAA peaks at higher concentrations. The fact that elevated MeHg are carried in the Pacific halocline suggests that high MeHg in these regions are more of an advected signal from OM remineralization in Chukchi Sea rather than local and recent ones, and the demethylation rates of MeHg might be slower than previously estimated. Another finding in this research is the high concentrations of MeHg in surface layer, including a second sub-surface peak close to the depth of subsurface chlorophyll maximum observed in many stations, and considerable MeHg found in surface water in a few stations. These results suggest that there might be another MeHg source in surface seawaters, which is most likely related to biological activities, and/or that photodemethylation in the surface ocean might not occur as fast as we previously thought.

WO-029

METHYLMERCURY MASS BUDGETS AND DISTRIBUTION CHARACTERISTICS IN THE WESTERN PACIFIC OCEAN

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Methylmercury (MeHg) accumulation in marine organisms poses serious ecosystem and human health risk, yet the sources of MeHg in the surface ocean remain uncertain. Here, we report the first MeHg mass budget for the Western Pacific Ocean estimated based on cruise observations (2012 and 2014 SHIPPO surveys). We found the major net source of MeHg in surface water to be vertical diffusion from the subsurface layer (1.8 to 12 nmol m-2 yr-1). A higher upward diffusion in the North Pacific (12 nmol m-2 yr-1) than in the Equatorial Pacific (1.85.7 nmol m-2 yr-1) caused elevated surface MeHg concentrations observed in the North Pacific. We furthermore found that the slope of the linear regression line for MeHg versus apparent oxygen utilization was about twofold higher in the Equatorial Pacific than the

North Pacific. This could be explained by redistribution of surface water in the tropical convergence-divergence zone, supporting active organic carbon decomposition in the Equatorial Pacific Ocean. Base on this study, we predict oceanic regions with high organic carbon remineralization to have enhanced MeHg concentrations in surface as well assubsurface waters.

WO-030

ASSESSING MERCURY BIOGEOCHEMICAL CYCLES IN THE GLOBAL OCEAN USING A 3D DYNAMIC MULTIMEDIA MODEL

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A number of numerical models have been developed to simulate the fate and transport of mercury in the global environment. Most of these models have been developed based on atmospheric general circulation models or air quality models. In these models, land/sea compartments are not explicitly considered, and inter-compartment transports are interpreted as secondary emissions. Integrated modeling of the atmosphere, ocean, terrestrial compartments, and biosphere is our prime focus. We developed a new global multimedia model called the Finely-advanced transboundary environmental model for mercury (FATE-Hg). In this contribution, we describe and evaluate the model, and discuss mercury biogeochemical cycles in the global oceans using the model. The outstanding features of our model are that 1) it is developed based on a coupled atmosphere-ocean transport sub-model and calculates transboundary transports both in the atmosphere and the ocean, including the deep ocean, with fine spatial and temporal resolutions (0.75°×0.75° horizontal resolution and 60 vertical layers in the atmosphere, 1.0°×1.0° horizontal resolution and 50 vertical layers in the ocean), 2) it implements a satellite-based ecosystem model, capable of estimating abundances and trophic structures of marine organisms and vertical carbon cycles through biological pumps, and 3) it considers production of methylated mercury in the water column followed by biotransfer from lower (i.e., particle organic matter) to higher (i.e., fishes) order consumers. The general chemical species of mercury and physical processes such as transformations in air, cloud water, seawater, and sediment; dry and wet depositions; and air-sea diffusive exchange of gaseous elemental mercury are also considered. We compiled monitoring data for mercury concentrations from peer reviewed literature to validate our results. We performed decadal simulation, and calculated the mercury budget in the atmosphere, ocean, sediment, and marine organisms. The result of the validation showed that our model could simulate levels and distributions of gaseous elemental mercury above the ocean, and dissolved elemental, reactive, and methylated mercury in the ocean.

WO-031

CONTRASTING TIMESCALES OF ANTHROPOGENIC MERCURY CYCLING IN DIFFERENT OCEAN BASINS

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Human activities like mining and fossil fuel combustion liberate mercury (Hg) sequestered in the lithosphere into biologically active surface reservoirs, where it can pose risks to human and ecological health. In our previous work, we showed that future trends in Hg concentrations and exposures are affected by the trajectory of past environmental releases due to the slow burial of Hg in coastal and deep ocean sediment. This work did not consider dynamics of ocean circulation and productivity specific to individual ocean basins that affect the lifetime and accumulation of Hg. Here we present a fully coupled 20-box biogeochemical model for the atmosphere, terrestrial ecosystems, and all major ocean basins globally. Global circulation between ocean basins is resolved using an ocean general circulation model (MITgcm) and exchange rates for Hg are constrained based on a synthesis of available ocean measurements. We find that the lifetimes of oceanic Hg are highly variable across basins, ranging from less than a decade for the upper Atlantic to hundreds of years in Pacific Deep Water. Results are highly sensitive to evasion rates, emphasizing the importance of resolving uncertainty in factors controlling ocean-atmosphere exchange of Hg0. We present an eigenanalysis of characteristic timescales that account for coupling between reservoirs and to track the fate of a pulse of atmospheric Hg through all environmental compartments. We use this analysis as the basis for examining potential responses in each ocean basin to future anthropogenic emissions trajectories. Previous atmospheric modeling without dynamic coupling to longer-lived terrestrial and oceanic reservoirs has shown only modest changes under future emission scenarios. Considering the legacy impacts in our fully coupled biogeochemical modeling framework by contrast suggests large increases in Hg deposition over all ocean basins relative to 2008 levels under business as usual emissions scenarios. In the North Pacific, seawater total Hg concentrations in 2050 relative to 2015 levels range from an increase of 40% under business as usual emissions to a decrease of more than 40% with zero anthropogenic emissions as a bounding scenario. Our results reinforce the benefits of global policies aimed at reducing emissions.

WO-032

GLOBAL FLOWS OF METHYLMERCURY FROM FISHERIES HARVESTS

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Human activities have greatly perturbed the natural biogeochemical cycle of mercury and released large quantitites of previously sequestered mercury into the oceans. Methylmercury (MeHg) is the only species that biomagnifies in aquatic food webs and is widely recognized as negatively impacting the behavioral and reproductive health of fish, marine mammals, and humans. The main objective of this work is to link previously modeled Hg deposition into the ocean and seawater reservoirs of Hg species to MeHg flows associated with harvests of commercially important fish stocks. We compare the most recent deposition estimates from the GEOS-Chem global CTM based on updated oxidant chemistry and modeled total and MeHg reservoirs (seawater and plankton) in the global oceans from the MITgcm, to reservoirs and flows of MeHg from commercial fisheries. Based on estimated fisheries catches between 2001-2010 from the Sea Around Us database, we construct a first estimate of MeHg levels in global ocean catches by fishing sectors (industrial, subsistence and artisanal) and taxonomic groups. For species without data on MeHg levels in their tissues, we use a regression model to relate Hg concentrations to trophic level and fish length. Results show domestic waters are the major source of MeHg for most world regions and industrial fisheries are the predominant sector transferring MeHg from fish in the global oceans to humans. We quantify in this work the proportion of the oceanic MeHg budget removed by fishery catches.

2b-3: Sources and cycling of mercury in freshwater ecosystems

WO-033

APPLICATION OF A NEW MATHEMATICAL FRAMEWORK FOR QUANTIFYING WATER-MEDIATED MATERIAL CONNECTIVITY TO IMPROVE UNDERSTANDING OF TERRESTRIAL MERCURY TRANSPORT

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Understanding the hydrological and biogeochemical controls on mercury mobility in terrestrial upland and wetland landscapes is imperative for accurately simulating terrestrial mercury inputs to aquatic ecosystems. Despite decades of research investigating the relationships between hydrological processes and the biogeochemical cycling of mercury, landscape heterogeneity is still a major source of uncertainty in generating reliable simulations of mercury transport to receiving waters across scales and landscapes. Within the hydrological community, the concept of hydrologic connectivity is viewed as an organizing principle that underlies landscape complexity. While the phrase biogeochemical connectivity has not been frequently used in a similar manner, many approaches to understanding diffuse pollution risk at the catchment scale have focused on sources and mobilization with a basic representation of the effect of connectivity between the landscape and receiving waters. Recently, a cohesive mathematical framework to quantify the occurrence, frequency, duration, and magnitude of hydrologic and water-mediated material connectivity has been proposed to bring these concepts together. Here, we show how this framework can be applied to better understand the hydrological and biogeochemical conditions necessary for inorganic mercury to be transported from forested upland catchments to receiving waters. By providing a means to detect, quantify, understand and model the water-mediated connectivity of material, such as mercury, across different landscape units, we demonstrate that this framework will also be useful for site inter-comparisons, as well as have the potential to inform environmental policy and management decisions that are dependent on quantifying connectivity.

WO-034

HYDROLOGIC AND BIOGEOCHEMICAL FACTORS AFFECTING SPATIAL AND TEMPORAL VARIATION OF METHYLMERCURY IN WATER, SEDIMENT, AND BIOTA IN A MANAGED FLOODPLAIN, NORTHERN CALIFORNIA, U.S.A.

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The Cache Creek Settling Basin (CCSB) is a 1600-hectare floodplain area in Yolo County, bounded by levees since its construction in 1937 and expansion in 1993. The CCSB traps sediment to reduce accumulation in the Yolo Bypass, a conveyance for Sacramento River flood waters to the SacramentoSan Joaquin Delta, protecting the city of Sacramento. The CCSB traps particulate mercury (Hg) eroded from the Cache Creek watershed, which has several natural and anthropogenic Hg sources: wastes from inactive Hg mines and gold mines where Hg-amalgamation was used historically, thermal springs, and erosion of geologic materials with naturally elevated Hg. Analysis of filtered water and suspended particulate samples for total mercury (THg) and methylmercury (MeHg)

in stream-flow entering and exiting the CCSB during 201016 indicated that: ~65% of particulate THg and MeHg were trapped in the CCSB; there was no net change in filtered-water THg load; and filtered-water MeHg load increased ~30% in basin outflows relative to inflows. The long-term average rate of sediment accumulation in the CCSB was ~2 cm/yr based on analysis of 137Cs in 6 cores. Principal habitats mapped within the CCSB were: open water (stream channels and canals), riparian (along stream channels), non-agricultural floodplain, and agricultural (row crops, primarily corn and tomato). Analysis of shallow sediment (02 cm) collected at 93 locations within the CCSB on four occasions during 201315 indicated that agricultural and open-water habitats had consistently lower MeHg than riparian and non-agricultural floodplain habitats, along with lower concentrations of total reduced sulfur (TRS) and organic matter. Within each habitat, there was a consistent increase along the direction of stream flow in MeHg concentration and the ratio MeHg/THg (%MeHg). A similar spatial variation was found for TRS and organic matter, which increased in the flow direction, and median grain size, which decreased. A similar pattern of increasing MeHg with downstream distance was found in tissue of western mosquitofish (Gambusia affini), for caged (30-day exposure) and uncaged samples. Monthly sampling of shallow sediment at selected sites during 201516 revealed increased MeHg during wetter conditions (December through May), and increased reactive Hg(II), a precursor to MeHg, during drier conditions (June through November). The finding that riparian and non-agricultural floodplain habitats had significantly higher MeHg than agricultural (row-crop) habitat could have broad implications for resource management, given that these habitats are typical of managed floodplains in the SacramentoSan Joaquin Delta region and elsewhere.

WO-035

EXPORT DYNAMICS OF RIVERINE MERCURY FROM GANGA ALLUVIAL PLAIN, NORTHERN INDIA

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India is the largest consumer (5.31 × 105 kg in 2002) as well as emits 3.10 × 105 kg mercury on large scale. It has gained scientific attention due to its increasing riverine mercury concentrations and discharges at its ocean margins. In northern India, high levels of mercury have recently been reported in rain (3.13 ppb), ground (15.58 ppb) and river water (9.9 ppb) as well as in fishes (152 ppb) and lichens (4112 ppb) of the Ganga Alluvial Plain. To understand the export dynamics of riverine mercury from the Ganga Alluvial Plain, the Gomati River (a 900-km long alluvial tributary of the Ganga River) was selected for the present study. The river drains 30,437 km2 area of the alluvial plain and experiences a warm and humid sub-tropical climate with four distinct seasons: the monsoon, the post-monsoon, the winters and the summer. Chandwak (25°35′N; 83°00′E) sampling site has been identified from distal part to represent the entire drainage area. Dissolved mercury (Hgd) flux in the Gomati River was obtained from the observations (n=36) of water discharge and Hgd concentration at an interval of ten days for the period of June 2009-May 2010.

The average Hgd concentration and flux were recorded during the monsoon (12.8 ppb; 3.73 × 104 kg) the post-monsoon (11.2 ppb; 2.06 × 104 kg), the summer (8.1 ppb; 0.79 × 104 kg) and the winter (6.9 ppb; 0.26 × 104 kg) seasons. The estimated annual Hgd flux was 6.84 × 104 kg to the Ganga River, out of which 85% move during the monsoon and post-monsoon seasons and strongly correlated to water discharge. It is two orders of magnitude higher than Yenisei, Ob, Mackenzie, Nelson and Yukon rivers of the Arctic region. Consequently, all alluvial rivers draining the Ganga Alluvial Plain potentially provide the major mercury to fishes of the Ganga River. Present study underscores the significance of mercury import from thermal power plants besides various anthropogenic sources (electrical wastes containing fluorescent lights, municipal solid wastes, medical wastes, brick kilns, agricultural and animal waste burning, phosphate fertilizer etc.). In the light of 'Minamata convention 2013', the transfer and implementation of advanced mercury abatement technology will be a promising way to reduce these mercury emissions. Future research must be a pursuit for the better understanding of impact of mercury on human health (such as cardiovascular disease) in this region which accounts for nearly 7% of world's human population.

WO-036

POTENTIAL IMPACTS OF CLIMATE CHANGE ON MERCURY TRANSPORT AND FATE ALONG THE CARSON RIVER-LAHONTAN RESERVOIR SYSTEM

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Historic mining practices have left the Carson River and Lahontan Reservoir (CRLR) system contaminated with high levels of mercury (Hg). Specifically, Hg levels in Lahontan Reservoir Sacramento blackfish (Orthodon microlepidotus) exceed federal consumption limits by nearly three-fold. Inputs of Hg to the system are mainly a result of riverbank erosion during high flow and diffusion from bottom sediments during low flow, and the relationships between streamflow and both mercury transport and bioaccumulation are non-linear. This research project attempts to predict the potential impacts of future climate change on the transport and fate (i.e., methylmercury concentrations in reservoir Sacramento blackfish) in the CRLR system.

The United States Bureau of Reclamation has produced future streamflow estimates for time period 2000-2099 for the upstream boundary of the modeled portion of the CRLR system using 112 CMIP3 climate projections and the Variable Infiltration Capacity (VIC) model. VIC results suggest that the hydrology of the system is likely to experience increased frequency of both high and low extreme flows, and the monthly averages of future flows are expected to be higher in the winter and lower in the summer compared to historical values. Predicted upstream river flow values are then used to drive the CRLR Hg transport model (RIVMOD, WASP5, and MERC4) that accurately predicts total and dissolved inorganic Hg along with total and dissolved methylmercury (MeHg) concentrations.

Bioenergetic algorithms and Hg mass balance approaches were combined into a single modeling framework (BioHg) to simulate the bioaccumulation of MeHg in Lahontan Reservoir Sacramento blackfish as a function of dissolved methylmercury (DMeHg) water column concentrations. Model parametrization relies on laboratory and field data to calibrate allometric coefficients related to consumption, respiration, specific dynamic action, egestion, excretion, and spawning. Actual consumption is reliant on feeding strategies, prey selectivity, filtering efficiency, and prey availability. BioHg is able to capture trends in observed growth and MeHg accumulation. The predicted Carson River flow patterns and associated DMeHg concentrations are then input into the calibrated BioHg model to compute potential future Hg levels in reservoir Sacramento blackfish. Predicted bioaccumulation levels increase in both the South (i.e., Upper) and Middle Basins of the reservoir as a result of an increase in DMeHg water column concentrations.

WO-037

THE BIOGEOCHEMICAL CYCLING OF MERCURY WITHIN LAKE POWELL, GLEN CANYON NATIONAL RECREATION AREA, U.S.A.

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Fish consumption advisories for mercury (Hg) are common in reservoir systems, including Lake Powell, a 300 km long reservoir along the Colorado River in the arid Southwest region of the U.S.. Based on striped bass Hg concentrations, the consumption advisory for Lake Powell is limited to the lower 70 km portion of the reservoir, although the reason for this spatial trend is unknown. This trend coupled with the fact that Hg biogeochemical cycling and bioaccumulation studies in reservoirs have been far more extensive in the eastern U.S., compared to the western U.S., promoted a two-year investigation of Lake Powell Hg dynamics. Samples of surface water (multiple depths from surface to bottom), seston and bed sediment were collected at 12-13 fixed sites during both minimally-stratified / high inflow (May/June 2014) and strongly-stratified / low-flow (August 2015) conditions. These samples were analyzed for a large suite of Hg and non-Hg related parameters. In-situ water column parameters were also measured in continuous profile from 24-25 sites during both sampling events. The totality of results supports a conceptual model in which the concentration and chemical nature of water column particulates transitions from a mixture of inorganic plus autochthonous (phytoplankton) and terrestrially derived organics in the upper end of the system to largely phytoplankton dominant in the lower portion of the system. This transition subsequently results in the deposition of more labile organic matter (phytoplankton) in the lower reservoir, which fuels higher rates of anaerobic microbial activity and higher rates of methylmercury (MeHg) production, which bioaccumulates up the food web and results in the higher observed Hg concentrations in striped bass in the lower portion of the reservoir. Specific supporting observations include increasing rates of microbial MeHg production and microbial biomass in sediment, increasing water column and seston MeHg concentrations, higher phytoplankton biomass, and decreasing fluorescent dissolved organic matter from the upper (riverine input) to the lower (towards the dam) regions of the reservoir. A distinct peak in water column MeHg (as a percent of total Hg) was routinely observed at or near the thermocline, suggesting the possibility of water column MeHg production in addition to benthic production. Molecular analysis of sediment suggests that the elemental sulfur and ferric iron reducing bacterial genus Desulfuromonas sp. may be the dominant microbe associated with MeHg production in Lake Powell.

WO-038

MERCURY IN AQUATIC ENVIRONMENT OF VIETNAM, RISK OF CONTAMINATION AND THE WAY FORWARD

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In Vietnam, mercury has been widely used in industrial production, particularly coal power plants, cement factories, steel plants. Industrial and municipal wastewater is directly discharged into many rivers, whereas the state control and monitoring of Hg has yet to be strictly, making Vietnam facing a high risk of mercury contamination to air and water resources.

In Hanoi capital, the largest city in the Red River Delta, there are more than 90 factories in the city, consuming nearly 148,000 tons of coal and 12,000 tons of petroleum per year, as a big source of mercury to be released to the environment. Analytical data of samples in two rivers (ie. Nhue river and To Lich river) in Hanoi capital revealed Hg concentrations of 0.09 - 3.34 µg/l in river water, 0.078 - 1.136 ppm in river sediment, and 0.036 - 1.567 ppm in suspended particulate matter (SPM), respectively, with a tendency to increase from upstream to downstream. Analytical results for water sample at river mouth of the Red River Delta also demonstrated that most of the Hg is transported into the estuary from upstream sources and Bach Dang river estuary is a significant source of MMHg during the dry seasons (3 g MMHg/day). During high river discharge in the wet season, there was a large estuarine input of total Hg while the longer residence time of the waters during the dry season promotes increasing MMHg formation. Even though high concentration of Hg has been detected to accumulate in water hyacinth, particularly at sampling site with high Hg concentrations detected in water and suspended particulate, there have yet data as evidence for impacts of Hg on human health. After joining the Minamata Convention on Mercury in October 2013, Vietnam has paid serious attention to monitoring, controlling and reducing mercury emissions, and as a way forward, more care on environmental health related to Hg should be taken, in further in-depth research and international collaboration.

WO-039

MERCURY AND METHYLMERCURY DISCHARGE FROM CHINESE RIVERS TO ADJACENT SEAS

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Methylmercury (MeHg) is a potent neurotoxin that threats aquatic environment and human health. Human activities can drive more total mercury (THg) and MeHg releasing from land to sea, and riverine pathway contribute the most. To better understand the source and contributions of global riverine THg and MeHg to seas, we quantified the THg and MeHg discharge from Chinese rivers to the adjacent seas, based on some measurements of the 16 largest rivers in Mainland China. Filtered water and suspended sediment were collected in four season of the 7 largest rivers, and dry and wet seasons of other 9 rivers. Both THg and MeHg were divided into dissolved phase and particulate phase, and the measurements followed the U.S. EPA Methods. Totally 80 tons of THg and 1.2 tons of MeHg discharge from rivers in Mainland China to the adjacent seas in 2015. Annual riverine THg discharge was decreasing in recent years, due to the management of Chinese government on Hg release from anthropogenic sources to aquatic environment. This study has provided more detailed information on THg discharge and filled the vacancy of riverine MeHg discharge from Chinese rivers to seas.

WO-040

USE OF HIGH-FREQUENCY OPTICALLY-BASED MEASUREMENTS TO ASSESS MERCURY CYCLING, TRANSPORT, AND FATE IN CONTAMINATED ESTUARINE AND RIVERINE SYSTEMS

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Understanding mercury cycling, transport, and fate is essential for assessing and managing water quality at aquatic sites where human influence may have affected natural processes. Water column and near-bed processes vary temporally and spatially due to physical processes such as tidal variability, storm flow events, and hydrodynamic interactions between different ecosystems within an impacted site. This system-wide variability confounds evaluation of mercury sources and transport mechanisms when using conventional laboratory-based analysis of discrete water samples. The OPTically-based In-situ Characterization System (OPTICS) provides for estimation of particulate and dissolved mercury and methyl mercury concentrations in surface water at high frequency (e.g., less than hourly) and over extended (e.g., order of months) durationsupporting efficient, cost-effective collection of an unprecedented amount of data to understand mercury variability and its relationship to the processes that drive mercury fate and transport.

Case studies are presented where OPTICS monitoring was employed to support the evaluation of mercury cycling, transport, and fate at an estuarine site and a riverine site. At the estuarine site, OPTICS data were integrated with physical, biogeochemical, and water quality measurements to demonstrate that marsh-derived organic matter settles to the waterway sediment bed during slack tides to form a thin, benthic layer of low-density material on which mercury and methyl mercury can be sorbed. Thin, benthic layer resuspension during high tidal velocities and storm flows is a primary mechanism for mercury and methyl mercury transport to surface water. Further, the OPTICS results demonstrated a net flux of mercury and methyl mercury from the waterways into the marshes, where the chemicals are retained. The OPTICS results are an important line of evidence to the conceptual site model (CSM), which forms the basis for the evaluation of a remedy for the site.

At the riverine site, OPTICS monitoring enabled evaluation of mercury transport under baseflow and storm flow conditions. Particulate mercury and methyl mercury transport was substantively increased during storm flow conditions due to bank interactions and resuspension of bedded sediment. Dissolved methyl mercury concentrations increased with increasing water temperature, likely due to increased microbiological activity. Baseflow patterns indicate a diurnal pattern potentially consistent with nocturnal bioturbation processes. The results of the pilot test were used to verify and refine the CSM and will be an important consideration to the adaptive management of the site.

2g-2: Legacy site assessment and management

WO-041

UNDERSTANDING MERCURY DYNAMICS AND OPPORTUNITIES FOR REMEDIATION AT THE HISTORICAL BLACK BUTTE MINE IN OREGON, USA

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The Black Butte Mine is a former mercury (Hg) mine in central western Oregon that is on the US National Priorities List due to off-site migration of mercury in surface water, and due to significant fish contamination in a nearby flood control reservoir. Two decades of environmental assessment and various remediation activities have been conducted at the site by state and federal agencies. This presentation provides an overview of the key findings from the environmental assessments to provide a holistic understanding of Hg transport pathways from the mine site, as well as methylmercury (MeHg) production in the downstream reservoir and accumulation in fish. At the mine site, water samples were collected from groundwater and surface water during baseflow and stormflow conditions for dissolved and particulate total mercury (THg) and MeHg. In the reservoir seasonal measurements of lake water column, sediment and porewater were collected for THg and MeHg as well as several ancillary parameters. The results for the water measurements at the mine site showed that surface water transport was the dominant pathway for offsite Hg mobilization, mostly through erosion during stormflow events. Peak stream THg concentrations reached 94,000 ng/L and mostly consisted of particulate-bound Hg. Downstream in the reservoir, there was large spatial variability in sediment THg concentrations (0.05 to 2.3 mg/kg) representing a range of influence from the upstream mine. Methylmercury production in the reservoir was also highly variable and was affected by variations in sulfate, organic carbon, and reservoir water level fluctuations. Fish Hg concentrations in the reservoir were up to 1.8 mg/kg. Overall, these results highlight the spatial and temporal variability in Hg transport and transformation from the mine site as well as impacts on a downstream fishery. These findings are being used to help guide upcoming remediation activities at the site.

WO-042

RELEASE OF MERCURY FROM MINE IMPACTED WATERSHEDS BY EXTREME EVENTS RESULTING FROM CLIMATE CHANGE

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An increase in intensity and frequency of extreme events resulting from climate change is expected to result in extreme precipitation events on both regional and local scales. These events have the potential to mobilize large volumes of mercury (Hg) in watersheds where mine wastes reside in flood plain deposits downstream from historic mines that operated with little or no environmental regulations. Most mine remediation has focused on mine sites and rarely have Hg contaminated flood plain deposits been evaluated or remediated. Several types of ore deposits have released Hg contaminated mine wastes that are now stored in flood plain deposits that extend from 10s to 100s of km from the mine site. These deposits have varying degrees of risk to release bioavailable Hg based on the volume, concentration, and speciation of Hg in the flood plain deposits. These mines include: 1) Hg and placer Au mines that have the highest potential to release bioavailable Hg from flood plain deposits during extreme events; 2) massive sulfide, sediment and hot spring type gold deposits that have moderate potential; and 3) porphyry copper and MVT deposits that have low potential. The various types of downstream aqueous environments receiving Hg contaminated mine wastes resulting from extreme events are an important factor to consider in evaluating the risk posed by extreme events in mine impacted watersheds. Reservoirs are at highest risk for a significant increase of MeHg in the food web after an extreme event because the Hg contaminated sediment also supplies sulfate, iron and organic carbon. Several reservoirs in the California Hg mineral belt have had a significant and rapid increase in MMeHg production that impacted the food web after Hg mine contaminated sediment was released into the reservoir.

An analysis of the Hg mine-impacted watersheds, where Hg is stored in contaminated flood plain deposits, in more than 50 Hg mines from the California Hg mineral belt, indicates that this Hg source poses a major environmental risk to aquatic systems during a period of climate change. An extreme Atmospheric River 1000 Storm (ARkStorm) similar to the 1861-1862 storms has the potential to remobilize Hg stored in flood plains throughout the entire Hg mineral belt and impact reservoirs, estuaries, and wetlands throughout much of California.

WO-043

WETLANDS ENHANCE METHYLMERCURY CONCENTRATIONS AT A LEGACY MINE SITE IN CENTRAL IDAHO, UNITED STATES

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The East Fork South Fork Salmon River (EFSFSR)is a critical spawning habitat for bull trout and Chinook salmon in central Idaho. Monthly water-quality monitoring on Sugar Creek, a tributary to the EFSFSR downstream from the Cinnabar mercury mine site, has demonstrated elevated mercury (Hg) concentrations, with the greatest concentrations occurring during peak snow melt in late May and during high-intensity summer thunderstorms. Mercury mineralization at the Cinnabar mine site is hosted by carbonate rocks, which generate waters dominated by Ca2+ and HCO3- at pH 7 to 9. Sampling along Sugar Creek and its tributary Cinnabar Creek was conducted near baseflow conditions to determine groundwater contributions to methylmercury (MeHg). Total unfiltered Hg concentrations in Cinnabar Creek increased from 8 to 14 ng THg L-1 above the mine site to 170 to 213 ng THg L-1 in the main reach flowing through the mine site. Unfiltered MeHg concentrations from same reaches of Cinnabar Creek increased from <0.04 ng MeHg L-1 to 0.07 to 0.15 ng MeHg L-1, or 0.03 to 0.09 percent of the total mercury, in unfiltered water from Cinnabar Creek flowing through the mine site. Groundwater seeps and mine adits were sampled to evaluate contributions from groundwater in direct contact with cinnabar-bearing carbonate rocks. There are several fault-controlled seeps with associated wetlands in the mine site with up to 960 ng THg L-1 and 6 ng MeHg L-1, reflecting the enhanced dissolution and methylation of mercury in these discrete areas of high organic matter in what is otherwise a low-nutrient watershed. Incorporating existing fault-controlled groundwater seeps into a remediation design is critical for reducing downstream transport of mercury and other metals in legacy mercury mine sites.

WO-044

TRACING HG MOBILITY AND DISTRIBUTION IN A HISTORICAL MERCURY MINING ECOSYSTEM: FROM CALCINE TO BULL TROUT AND SAMPLES IN BETWEEN

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Persistent mercury (Hg) impact from legacy mines continue to present risk to the environment and human health globally. The Stibnite Mining District is a historical mining area located near the headwaters of the East Fork South Fork Salmon River in central Idaho. Past mining of antimony, gold, silver, mercury and tungsten from the early 1900s to the 1990s has resulted in elevated Hg as well as other trace elements in the surrounding ecosystem. The Cinnabar and Fern legacy Hg mine sites, within the Stibnite Mining district are primary source areas for elevated Hg entering the ecosystem. The extraction of Hg from cinnabar was carried out via two methods over the 45 years of Hg production in this mining district: 1) Hg was initially retorted in rotary kilns (1921 to 1956), a process during which the ore is heated to 500-600°C volatizing the Hg to gas with recovery as elemental Hg(L) via condensation and 2) Hg was later produced by wet flotation and electro-separation (1956 to 1966). These distinct methods of extracting Hg from cinnabar resulted in variations of Hg concentration and isotopic composition being introduced into the environment during the active processing of the Hg ore, as well as long term legacy input of Hg from the weathering of calcine tailing piles and other residual Hg contamination sources related to the original mining and processing of Hg ore. Mass dependent fractionation of Hg isotope ratios and variation in Hg concentrations resulting from the processing of cinnabar ore has been reported previously for produced Hg metal and residual waste fractions (Hg(L), Hg(g), and calcines). These Hg fractions possess the potential of releasing Hg into the local environment over sustained periods of time. In order to better understand Hg behavior in legacy mining areas, establish a priority of effort for remediation, and determine differences in mobility and bio-accessibility of Hg sources in this ecosystem, we investigated Hg concentrations and isotopic compositions in a wide range of samples: two distinct calcine produced tailing piles, lichen, periphyton, stream sediment, soil, tadpoles, tadpole eggs, tailed frog, sculpin, and bull trout. We will present Hg concentrations and isotopic compositions of samples collected over multiple years within the mining district and provide a post-mining baseline of Hg distribution. This baseline will help inform environmental assessments for future landuse activities, including recommencing of mining operations and onsite remediation in this ecosystem.

WO-045

CLIMATE INFLUENCES ON IMPORTANCE OF LEGACY SITES AS MERCURY SOURCES ON THE WATERSHED SCALE

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The Cache Creek watershed, located in the coast range of California, has had a legacy of mercury (Hg) mining. Hg levels in Cache Creek are elevated above regional background; Cache Creek exportstotal Hg (THg) and methylmercury (MeHg) to the San Francisco Bay Delta.The regulatory approach for controlling Hg in the Cache Creek watershed finalized in 2007 focused on reductions in THg loading from legacyHg mines in tributaries (e.g., Harley Gulch). The Hg mines in Harley Gulch were remediated in 2007, reducing loads from the mines by 95%. However, an analysis of fish tissue THg data conducted in 2015 has indicated thatHg concentrations in fish tissue THg collected from Cache Creek in 2011 were not declining. The regulatory agencies responsible for implementing the Hg control approach haveconcluded that additional remediation of Hg mines in the CacheCreek watershed will be required for water quality to improve.

A recently-completed data synthesis and comprehensive evaluation of Hg sources and cycling in the Harley Gulch watershed indicates thatfurther efforts to remediate Hg mines may not result in the attainment of local water quality targets oralter Hg levels downstream. This isdue to the presence of natural Hg sources inHarley Gulchandthe weak hydrological linkage between Hgmines in Harley Gulch and Cache Creek. Surface water and sediment data collected pre- and post-remediation of the mines in the vicinity of Harley Gulch has revealed that the remediation has successfully prevented the erosion of high THg concentration particles but aqueous MeHg targets have not been met. Additional Hg mine remediation is likely to have spatially limited benefit due to the nature of Hg transport in the watershed. The presence of naturally occurring sources of Hg in Harley Gulch, including connate groundwater and high THg concentration soil unimpacted by mining activities may prevent attainment of water quality objectives locally in Harley Gulch. Harley Gulch is an ephemeral stream and Hg loading even from un-reclaimed mine sites is limited to erosion of THg adsorbed to particles or in calcine wastes during rain events, which generally occur between October and May.The THg loading from historical mines is likely to be further reduced by climate change, which is predicted to lead to lower precipitation amounts in the ecoregion.Harley Gulch presents a case for why focusing on legacy Hg sites in complex watersheds may not lead to water quality improvements.

WO-046

SEDIMENT AND MERCURY LOADS TO HUMBUG CREEK: A SIERRA NEVADA TRIBUTARY IMPACTED BY THE MALAKOFF DIGGINS HYDRAULIC MINE

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Mercury contaminated sediment from legacy gold mines in the Sierra continues to be a source of inorganic mercury (Hg) to the environment. The discharge from Malakoff Diggins, once one of the largest hydraulic mines in California, is a source of Hg and sediment to Humbug Creek. The purpose of this study was to estimate the load of particulate bound Hg and suspended sediment in Humbug Creek for Water Years 2012 and 2013. Grab samples were taken from baseflow conditions and from multiple storm events and analyzed for nonfiltered Hg, filtered Hg and total suspended sediment (TSS) (EPA 1669, EPA 1631, EPA 160.2). A stage discharge relationship was developed for the Humbug Creek gage station over a range of flow conditions. Samples were collected from Humbug Creek upstream of the Malakoff Diggins discharge point, from the discharge point and downstream of the discharge and Humbug Creek confluence at a stream gage. The annual load in Humbug Creek for suspended sediment and particulate bound Hg was calculated at the gage using relationships established with continuously monitored turbidity (15 min data) and grab samples of total suspended sediment (n = 25, R2 = 0.82) and particulate bound Hg (n = 15, R2 = 0.80). The annual load was 100-120 grams of particulate bound Hg and 475,000-575,000 kg of suspended sediment. For both water years, as much as half of the annual sediment load was from a single storm event during which 3-4g of particulate bound mercury was released per day. The contribution of mercury loads from legacy hydraulic gold mines should be quantified as it is a critical source control strategy for California Total Maximum Daily Load programs.

WO-047

LEGACY MINING MERCURY RELEASES IN A RECOVERING WETLAND LANDSCAPE (UPPER PENINSULA, MICHIGAN)

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A century ago the Upper Peninsula of Michigan was a major industrial region, centered on mining. Several regional ores contain natural mercury (gold, silver, copper, zinc, massive sulfide ores) and mercury was imported for localized gold and silver operations. Mining activities released mercury in tailings and in copper smelter and iron furnace-taconite operations. Modern NADP estimates of atmospheric mercury deposition range from 4-10 µg/m2/yr (wet) to 5-30 µg/m2/yr (gross). However, in the neighborhood of mining operations, total mercury fluxes from lake sediment cores record greatly enhanced loading (mean ca. 1590 µg/m2/yr; peaks of 5120 to 21,300 µg/m2/yr) during the height of copper mining (1880-1968). Methylmercury profiles document methylation during active mining, and 20-40 yr time lags for deposition of MeHg after operations. Here we also discuss the high regional concentrations of mercury in fish. In the region, mining-disturbed lake sediments possess higher THg and MeHg mercury concentrations. There are also regional correlations with DOC. We argue that legacy mining enrichments are juxtaposed upon a regional pattern of recovering wetlands and that both factors (forest and wetland recovery, mining legacy effects) probably contribute to the regionally elevated methyl mercury levels in fish.

WO-048

CAN NATIVE PLANT SPECIES IN COMBINATION WITH A LOW-DOSE SELENIUM (SE) ADDITIVE BE USED FOR PHYTOSTABILIZATION OF MERCURY (HG) AND ARSENIC (AS) CONTAMINATED MINING WASTE?

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Many historical gold mining sites across the world are contaminated with mercury (Hg) and other potentially toxic elements, such as arsenic (As). The high level of Hg is due to the gold extraction process (mercury amalgamation) used in the late 1800`s to early 1900`s. Mercury amalgamation is still used at artisanal mines in developing countries and at smaller mines, due to its simplicity. The waste from this process, tailings, presents significant human health and ecological liabilities. Revegetation of tailing deposits could provide increased protection against wind erosion, toxic dust blowing across populated areas and prevent leaching of Hg and As into waterways. A recent Saint Marys University study demonstrated that growth of a reclamation grass seed mix in highly contaminated gold mine tailing material can be facilitated by low-dose selenium additions. However, commercial reclamation seed mixes often include non-native highly-invasive species which should be avoided. There are several advantages to using native plant species for reforestation and reclamation, including proven hardiness in growing regimes, avoiding introduction of new invasive species in vulnerable ecosystems, and maintaining / improving the biodiversity of impacted ecosystems. The objective of this project was to (1) identify wide-spread established native species which can be used in phytostabilization of gold mine sites, (2) assess whether seeds of native hardy species can be used directly in exposed tailing deposits to promote natural revegetation, and (3) assess if a low-dose of sodium selenite can promote growth of native species while limiting the plant bioaccumulation of Hg and As. Three widespread North American native plant species were selected for this study: Panicum virgatum, Juncus tenuis and Anaphalis margaritacea. Plants were grown in 7 replicates of untreated tailing material, 7 replicates of Se treated tailing material (3 mg Se/kg) and in 7 replicates of artificial soil (control) for nine weeks. The results from this study are currently being compiled and are promising; indicating that seeds of native hardy species can be used for cost-effective phytostabilization of tailing deposits. In addition, preliminary results indicate that a low dose of sodium selenite increased the biomass, % emergence, shoot height and root length in Juncus tenuis, increased % emergence in Anaphalis margaritacea, and increased root lengths in Panicum virgatum. The sodium selenite additive also decreased plant shoot accumulated [Hg] in Panicum virgatum by 36%. Accumulated Hg concentrations in Anaphalis margaritacea shoots did not differ significantly between untreated and Se treated tailings.

2h-1: Mercury cycling in response to ecosystem perturbations

WO-049

CLIMATE CHANGE EXACERBATES MERCURY BIOACCUMULATION IN A MARINE FOOD WEB FROM THE NORTHEASTERN PACIFIC: INSIGHTS FROM AN ECOSYSTEM MODELLING APPROACH AND FOOD SAFETY IMPLICATIONS

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Global contamination by anthropogenic mercury is an issue of great concern as highlighted by the Minamata Convention on Mercury. The organic form of mercury, methylmercury (MeHg), is a ubiquitous, bioaccumulative and toxic contaminant that biomagnifies in marine food webs, exhibiting the highest concentrations in apex predators. In the face of climate change, ocean warming and acidification may potentially intensify methylmercury bioaccumulation in food webs with implications for food safety and public health. Several studies suggest that climate change is already changing pollutant fate and transport in the ocean, and affecting pollutant exposure and accumulation in marine organisms that can subsequently result in adverse effects on ecosystem and human health. However, the interplay of the combined effect of climate change and methylmercury exposure and bioaccumulation has been rarely quantified. Using an ecosystem modelling approach (EwE model with the Ecotracer module), we simulated potential future scenarios for mercury bioaccumulation in a regional food web (i.e. Chinook salmon-resident killer whale food web from the Northeastern Pacific, including British Columbia, Canada and Washington State, USA) under climate change forcing, including Representative Concentrations Pathway (RCP), i.e. RCP 2.6 = strong climate change mitigation (low CO2 emissions), and RCP 8.5 = business as usual (high CO2 emissions). The outcomes were compared against a baseline scenario (no climate change forcing). The model simulations showed that MeHg bioaccumulation in the food web is exacerbated by ocean warming and acidification. In comparison to the baseline scenario, the percentage increase in mercury concentration accumulated in Chinook salmon is 1% and 10% under RCP 2.6 and RCP 8.5 scenarios, while in it is 1% and 8% in killer whales, respectively. The bioaccumulation simulated by the model echoes the importance of mercury uptake rates, which are faster in salmon relative to that in fish-eating killer whales; with the latter having a slower elimination rates. This level of bioaccumulation would have negative effects on all seafood consumers, but considering that seafood consumption by coastal First Nation communities from British Columbia is 15 times (64% of consumed seafood is salmon) that of the average Canadian consumers, Indigenous people will be exposed to much more mercury in comparison to non-Indigenous people in the long-term. The socio-economic implications of mercury-contaminated salmon fisheries intensified by climate change are discussed. This study improves our understanding of the interactions of climate and pollution impacts of multiple human stressors, highlighting key areas for concerted research and potential mitigation policies.

WO-050

METHYLMERCURY IN A WARMING ARCTIC OCEAN

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Rapid warming in the Arctic has resulted in unprecedented occurrence of ice-free waters and opportunities for new commercial fisheries. Global mercury (Hg) emissions from anthropogenic sources have greatly enriched levels of the toxic and bioaccumulative monomethylmercury (MeHg) in global marine food webs. Higher levels of MeHg have been reported in many Arctic food webs than at mid-latitudes and enrichment of tissue burdens across a suite of biota have been estimated at greater than 10-fold the pre-industrial levels. Most of this increase has been attributed to anthropogenic pollution but these prior analyses have not evaluated the contribution of changing ocean biogeochemistry. Climate related warming in the Arctic is nearly double that of mid-latitude ecosystems, leading to melting sea ice and permafrost, warmer seawater temperatures, higher freshwater discharges and marine productivity. Previous GEOS-Chem modeling has suggested reduced sea-ice cover will lead to increased oceanic evasion of elemental Hg (Hg0) and lower total Hg concentrations but the implications for MeHg production have not been explored. The overall result of these conflicting effects on MeHg levels in commercially important fish species is unknown. Here we construct a biogeochemical model (MITgcm) for the Arctic that combines cycling of MeHg and uptake into biota. We use new measurements from the central Arctic basin in 2015 to experimentally evaluate the role of changing temperature, productivity, and light for production and degradation of MeHg in Arctic Ocean seawater, sea ice and food web. Modeled fish MeHg levels are most sensitive to changes in temperature and diet shift; we find that a 1°C rise in seawater temperatures can lead to a 30% increase in MeHg content of some important commercial fish species despite a significant reduction in global Hg emissions.

WO-051

METHYLMERCURY DYNAMICS IN A SULFATE-IMPACTED WATERSHED

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Areas of the St Louis River watershed in northern Minnesota have been chronically impacted by sulfate loading from iron mining for over a century. Multiple studies were conducted on several natural systems over a wide range of sulfate concentrations to assess the effects of elevated sulfate loading on Hg dynamics, methylmercury (MeHg) bioaccumulation and Hg methylation. Chronically sulfate-impacted systems were characterized by high sulfate (100s to 1000s ppm) in the water, high dissolved magnesium, low solid-phase Fe:S ratios, and elevated dissolved sulfide in sediment porewater. However, the high sulfate systems were not systematically elevated in MeHg in the water, sediment, or biota (dragonfly larvae). In a principal component analysis of surface water measurements in the St Louis River, sulfate concentrations were associated with magnesium concentrations while dissolved MeHg concentrations grouped with Fe, DOC, and THg concentration. This finding is consistent with MeHg, THg, DOC, and Fe being delivered primarily via watershed inputs while Mg and sulfate are discharged from mining activities. MeHg in stream-dwelling dragonfly larvae were correlated with dissolved MeHg concentrations over a wide range of sulfate concentrations during two relatively high flow years where MeHg inputs from local watersheds appeared to dominate over any in-stream MeHg transformation processes. Dissolved and solid-phase MeHg concentrations in lake and wetland sediment in the watershed were statistically similar across sulfate-impacted and un-impacted systems. Chronically sulfate-impacted systems had significantly lower potential methylation rates compared to sulfate-limited systems due to accumulation of dissolved sulfide which limited long term MeHg accumulation, perhaps as a result of less bioavailable Hg-S complexes or enhanced partitioning of MeHg into the aqueous phase. These studies were conducted during relatively high flow conditions in which non-point source, precipitation-driven mobilization of MeHg from the landscape appear to have overwhelmed any potential impacts of chronic sulfate loading on Hg methylation and MeHg bioaccumulation in near-stream areas. In wetland and lake sediments, iron and water level fluctuations were identified as key controls on the extent to which sulfate and sulfide impact sediment MeHg production and accumulation. Further research is needed to determine how MeHg in sulfate-limited freshwater systems might respond to initial increases in sulfate loading and how iron and sulfur loads interact to define porewater sulfide and Hg bioavailability; however, chronically impacted systems do not appear to continually accumulate or produce MeHg at rates different from un-impacted systems in the St Louis River watershed.

WO-052

EUTROPHICATION AND ALGAE BLOOMS MAY HAVE SIMILAR EFFECTS ON METHYLMERCURY ACCUMULATION AT HIGH ALTITUDE SULFATE-RICH ENVIRONMENTS

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Methylmercury (MeHg) is a well-known neurotoxic that bioaccumulates and biomagnifies through the food web and the factors that control its production and accumulation remain an important and complex question. Eutrophication is widely believed to stimulate mercury methylation and MeHg accumulation, while algae blooms are thought to reduce MeHg accumulation due to a dilution effect. Here we present data from a unique environment located in the tropics but at an altitude of more than 3800 m above the sea level. The emblematic Lake Titicaca is also naturally enriched with sulfate (frequently above 200 mg L^{-1}) and partly polluted with domestic and industrial wastewater mainly at Cohana Bay (DOC up to 6.1 mg L^{-1}). The gradient of eutrophication among different locations of the lake served as a natural experiment scenario. As expected we found an increased concentration of MeHg in more eutrophic compartments (> 60% of MeHg) than in more oligotrophic compartments (< 10% of MeHg) of the same lake. Such difference is in agreement with the hydrogen sulfide concentrations found close to the sediments and mainly produce by sulfate reducing bacteria (nearly complete inhibition of H2S production with molybdate), which increases with eutrophication and may reach more than 2 mg L^{-1} in water overlying sediments. Therefore, the most likely explanation would be that eutrophication increases MeHg production by stimulating sulfate-reducing bacteria and possibly by attenuating UV radiation-mediated demethylation effect, which is critical considering the high altitude of the system. Surprisingly, something very similar was observed during a massive algae bloom in April 2015. Hydrogen sulfide production increased significantly (up to 155 μg L^{-1} in surface waters) as well as MeHg concentrations through the lake by a factor of up to 40%. The algae bloom was located in the first 10 cm of the water surface, blocking light penetration and probably MeHg photodemethylation, while reducing oxygen saturation in the water column from more than 100% to 40% during the day. Such oxygen concentrations were likely lower during the night and may have allowed microbial sulfate reduction through the water column and the consequent increase of methylmercury production. The main algae of the bloom (Carteria sp.) is known to produce appropriate electron donors for sulfate-reduction. Consequently the particularities of this environment allowed the stimulation of MeHg production and inhibition of photodemethylation to overcome any dilution effect associated to the algae bloom. The degree in which our results can be extrapolated to other sulfate-rich environments is uncertain, but to our knowledge this is observed in natural environments and may have important implications regarding the management of sulfate-rich and mercury polluted environments.

WO-053

MERCURY DISTRIBUTION AND FLUXES IN THE CENTRAL EUROPEAN MOUNTAINOUS LAKE ECOSYSTEM SEVERELY DAMAGED BY THE BARK BEETLE INFESTATION

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The central European lake district extends within the Bohemian forest and Bavarian forest Mountains. It includes 8 glacial lakes whose catchments were strongly acidified in the 70 and 80s of the 20th century. The lakes in altitudes from 935 to 1087 m a.s.l. have been oligotrophic and prevailing tree species within the lake catchments was Norway spruce (Picea abies).

The research was mainly focused on Plešné lake (PL) catchment located at 1087 m .a.s.l. covering area of 0.67 km2. In 2004, forest at PL catchment was infested by the bark beetle (Ips typographus) and 88%–99% of trees had died by 2011.

To assess changes in Hg distribution within the soil profile due to forest dieback we compared the soil data from year 1999 with the situation in 2015. While the mean Hg concentrations in the O horizons decreased from 424 to 311 μg/kg, in A horizons the situation was reversed and we detected increase from 353 to 501 μg/kg. The means of Hg concentration in mineral soil remained relatively similar at 145 and 121 μg/kg. The increase in Hg concentrations within A horizons was concurrent with increase in organic C from 24.5% in 1999 to 39.9% in 2015. But the Hg/C ratio in the A horizon remained rather comparable (1.27 and 1.47). In O horizons Hg/C ratio decreased from 0.9 to 0.5 comparing 1999 and 2015 due to changes in litterfall composition and overall deposition due to canopy absence since 2005.

Tributaries, lake water and precipitation solutes were assessed to estimate the fluxes of Hg within lake catchment. In hydrological year 2016, mean annual Hg concentration in bulk precipitation reached 3.0 ng/L and bulk annual Hg deposition amounted at 4.6 μg/m2. PL water contained on average 4.4 ng/L of Hg and 8.2 mg/L of DOC. Mean annual Hg concentration in four lake tributaries ranged from 2.0 to 16.5 ng/L. The differences in Hg concentrations among individual streams were driven by DOC concentrations ranging from 2.1 to 21.2 mg/L.

The financial support was provided by the Czech Science Foundation project No. GA16-14762S.

WO-054

THE EFFECT OF WILDFIRE ON STREAM MERCURY AND ORGANIC CARBON IN A SOUTHERN APPALACHIAN FORESTED WATERSHED IN THE EASTERN UNITED STATES

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Wildfires alter forested ecosystems, which include large stores of mercury (Hg) and organic carbon, two compounds that are closely linked in vegetation, terrestrial soils and streamwater. Studies have shown that wildfires release elevated levels of mercury to the atmosphere which can be locally redeposited and subsequent to fires, charred organic material (vegetation and litter) remains on the soil surface. Both of these new fire-altered sources of Hg (and carbon) have the potential to be mobilized into lakes and steams, particularly during high-flow precipitation events.

However, no studies have conducted a detailed evaluation of mercury and carbon concentrations and dynamics in streams immediately following a wildfire.

This study investigates the coupled transport of mercury and carbon at Twomile Run, a headwater stream located in the forested mountains of Shenandoah National Park, in the year following a wildfire (April 16-May 2, 2016) which burned the entire watershed. Since June 2016, we have been collecting weekly baseflow samples and bi-hourly high-flow samples during storm events. Samples are analyzed for dissolved and particulate mercury (HgD and HgP, respectively), dissolved organic carbon (DOC), UV absorbance at 254 nm (UV254, surrogate for DOC character), total suspended solids (TSS), and volatile solids (VS). The chemical concentrations and dynamics will be compared to those in control streams, located in nearby catchments that were not burned in the fire. Initial evaluation of summer and fall stream samples indicate that, under baseflow and high-flow conditions, HgD concentrations and the HgD:UV254 ratio are similar to those observed in the unburned streams (DOC data not yet evaluated). Under baseflow conditions, HgP concentrations and the HgP:TSS ratio are also similar to those measured in the unburned streams. However, under high-flow conditions, HgP is approximately an order of magnitude higher per unit of TSS and VS and the HgP:TSS ratio is relatively unstable as compared to those observed in the unburned streams. These initial findings illustrate the variable response of this forested headwater system to wildfire disturbance. We will continue to collect and evaluate stream samples in the winter and spring to quantify mercury and carbon dynamics over the full range of discharge conditions, gaining a more comprehensive understanding of the impact of wildfire on downstream Hg and carbon transport. These findings will provide insight into how Hg cycling might change in the future, as wildfires are expected to increase, specifically in the mid-latitudes, with climate change.

WO-055

ATMOSPHERIC DEPOSITION OF MERCURY TO THE GREAT LAKES REGION UNDER FUTURE GLOBAL CHANGE SCENARIOS

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Following its emission through anthropogenic activities, mercury is transported globally through the atmosphere, deposited, and impacts local ecosystems as a result of methylation and bioaccumulation in food webs. We are studying potential atmospheric mercury contamination of the Great Lakes region and examining the extent to which local, regional and global regulation of emissions are required to bring deposition to desired levels. This study is part of a larger integrative study examining scenarios of mercury contamination of Great Lakes Region fish. Previous studies have shown that deposition has increased roughly three-fold above pre-industrial levels in this region. The global 3-D chemical transport model GEOS-Chem has been applied to estimate future atmospheric deposition rates of mercury in the Great Lakes region for selected future scenarios of emissions, climate, and land use/land cover. Three scenarios (aspirational, policy-in-action and failure-to-govern) reflecting varying levels of policy actions taken at the regional and global scales to curb anthropogenic mercury emissions are considered. Future changes in climate, land use/land cover and biomass burning emissions are estimated following the IPCC A1B scenario. Changes in biomass burning emissions reflect future alterations in fuel type and availability (land use/land cover), fire meteorology (climate change), ignition agents and anthropogenic suppression of fires in the region. We find that, assuming no changes in climate, annual mean net deposition flux of mercury to the Great Lakes Region may increase by approximately 32% over 2005 levels by 2050, without global or regional policies addressing mercury, air pollution, or climate. In contrast, we project that the combination of global and North American action on mercury could lead to a 21% reduction in deposition from 2005 levels by 2050. U.S. action alone results in a projected 18% reduction over 2005 levels by 2050. We also find that, assuming no changes in anthropogenic emissions, climate change and biomass burning emissions would, respectively, cause annual mean net deposition flux of mercury to the Great Lakes Region to increase by approximately 5% and decrease by approximately 2% over 2000 levels by 2050. Changes in land use/land cover are expected to cause no net change in mercury deposition to the region in 2050.

WO-056

HOW MULTIPLE ENVIRONMENTAL FACTORS AFFECT THE BIOACCUMULATION OF MERCURY

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Mercury (Hg) is a widespread global pollutant and neurotoxin that bioaccumulates and biomagnifies in aquatic food webs. Humans are most frequently exposed to Hg, particularly the more toxic form methylmercury (MeHg), through consumption of marine fish. Therefore, it is important to understand the environmental factors that influence bioaccumulation of mercury and how changes in climate will alter the fate of Hg in marine food webs. Environmental conditions that are predicted to change with climate include increases in temperature, precipitation, nutrient and carbon loading, and freshwater influx. Here, we used the estuarine amphipod, Leptocheirus plumulosus, to conduct single factor laboratory experiments to investigate the effects of organic carbon, temperature and salinity on Hg and MeHg bioaccumulation in amphipods feeding in estuarine sediments. In addition, we examined how the interaction of temperature and carbon impacted bioaccumulation in amphipods using two-factor experiments. Current results indicate that salinity had a slight impact on bioaccumulation of Hg, bioaccumulation of Hg increased as organic carbon decreased, and Hg bioaccumulation increased as temperature increased. However, we found no significant temperature carbon interaction. A biogeochemical model of Hg in sediments has been developed to predict the net effect of climate change on mercury bioaccumulation in marine organisms.

3a: Risk/benefit communication related to fish and seafood consumption

WO-057

NEW FDA-EPA ADVICE ABOUT MERCURY AND EATING FISH

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FDA and EPA have issued updated final advice on fish consumption. The advice updates the 2014 draft consumption advice and recommends that women who are pregnant (or might become pregnant) or nursing and young children eat certain amounts and types of fish in order to improve health and developmental outcomes while minimizing risk from methylmercury in fish. Since fish species vary in the extent to which eating the fish poses a risk of methylmercury exposure to the consumer, FDA and EPA developed recommended consumption frequencies to minimize the risk from methylmercury exposure while encouraging fish consumption. The advice graphically shows fish separated into three categories: Best Choices to be eaten 2-3 times a week, Good Choices to be eaten once a week only, and Fish to Avoid which the agencies are recommending the target audience of women of childbearing age and young children not consume. Accompanying Qs As are grouped in sections on the use of the chart, serving sizes, consumption by children, nutrients in fish, contaminants in fish, specific information on tuna, fish caught by family and friends, and other tips on eating fish. The advice and other related documents are available on the agencies websites at www.fda.gov/fishadvice and www.epa.gov/fishadvice.

WO-058

THE DIETARY GUIDELINES ADVISORY COMMITTEE, THE DIETARY GUIDELINES FOR AMERICANS, AND CONSUMER ADVICE ABOUT FISH

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The 2015 Dietary Guidelines Advisory Committee report recommends the consumption of seafood by pregnant women, following a similar recommendation by the 2010 DGAC. That advice is based on the exceptionally well grounded evidence for the need for certain nutrients, principally long chain omega-3 fatty acids, as the structural material required to develop a proper brain. Unlike most other foods, the DGAC focused on nutrient composition as a key issue, emphasizing the practical difference between nutrients in farmed versus wild fish induced by intensive feeding practices. It also emphasized the importance of minimizing environmental pollutants. The DGAC report is a technical document written to translate science to implications for practice. The Dietary Guidelines for Americans report is written based on the DGAC report and input from the public including industry. The DGA is then translated by practitioners such as registered dieticians to advice to the level of the consumer. The average consumer uses the words beef, pork, chicken, and pork to refer to single species, but uses the word fish (aka seafood) to refer to all sea animals, perhaps 100 species. Translation of nutrition advice to women of childbearing age must use consumer words that can be reliably implemented by, for instance, pregnant teenagers. Recommendations that distinguish between types of a particular fish (e.g. albacore vs light tuna) is lost on most consumers and leads to avoidance of all tuna. Advice which has been proposed to distinguish between subspecies of similarly named fish (e.g. bigeye vs skipjack tuna) that are seldom even identified on a product label is impossible even for the most careful consumers to reliably implement. The food selections that consumers make in the marketplace are a decision between one dish and another, though most scientific studies treat fish like an optional vitamin pill that may, or may not be consumed, rather than a food that will substitute for another food. Advice from the DGAC is simple: eat a variety of fish and seafood, 8-12 oz per week. Integrating this advice with the evidence that Americans consume excess red meat leads to the simple message to substitute 2-3 dishes per week with fish.

WO-059

UTILITY OF QUANTITATIVE RISK/BENEFIT ANALYSIS IN DEVELOPING FISH CONSUMPTION ADVISORIES

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Initially fish consumption advisories focused upon a toxic constituent in fish to ensure that consumers were not exposed to greater than some daily dose limit of that constituent (e.g., the USEPA reference dose or RfD). This focus on risk avoidance created a potential loss of benefits since the predominant source of certain nutrients such as omega-3 fatty acids (O-3 FAs) is fish. We have been developing a quantitative risk/benefit model that provides an estimate of the net effect of positive and negative constituents in fish. Given that the focus of many fish advisories is on the potential for methyl mercury (meHg) to adversely affect neurodevelopment from prenatal exposure, our modeling has evaluated the counterbalancing effects of meHg and O-3 FAs on brain development. Using dose-response slopes for the benefit of O-3 FAs and the risk of meHg we have been able to simulate the net effect of fish ingestion on neurodevelopmental outcomes, with specific focus on visual recognition memory (VRM), an early life indicator of IQ. This quantitative modeling approach has enabled the evaluation of both locally caught and market purchased fish species based upon datasets describing the O-3 FA and Hg content of these species. The implications of such an approach for fish consumption advisories are that: 1) it provides a tool to evaluate the health effects of fish consumption in addition to the meHg RfD (risk only approach); 2) it provides an evidence-based rationale for advising greater fish consumption in those cases where in spite of the presence of meHg, the modeling predicts a clear benefit; 3)it allows for ready comparison of risks and benefits across seafood choices; and 4) it provides a framework for evaluating fish that can be improved as new toxicology/epidemiology data are gathered for these and other fish constituents. This presentation will compare this modeling approach with those developed by FAO/WHO, the USFDA and others, it will provide a framework for incorporating quantitative risk/benefit modeling information into the setting of consumption advisories, it will discuss the implications of the modeling for specific market purchased fish species, and it will highlight the uncertainties and data gaps which still limit its utility. Key among these are aspects of fish that may provide benefits and risks that are not captured by the focus on only two constituents (O-3 FAs and meHg). Recent efforts to expand the model to capture the neurodevelopmental risks associated with PCBs and the benefit from other constituents in fish will be described.

WO-060

SUCCESSFUL DIETARY RECOMMENDATIONS REGARDING MERCURY IN A HIGH EXPOSED COMMUNITY

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High levels of Hg in meat and organs from pilot whales, which are an important traditional food source for the Faroese were first reported in 1977. This finding led to the first consumption advisory for the general Faroese population from the Chief Medical Officer to limit the consumption of pilot whale to one meal per week and to completely avoid pilot whale liver and kidney. Since 1980, pregnant women were specifically advised to limit their consumption of pilot whale meat and blubber. In 1989, additional information on high levels of organochlorine contaminants in the blubber of pilot whales led to the consumption advisory that not more than 200 g of whale meat and blubber (each) should be consumed per month, and that liver and kidney should be avoided completely. In 1998, another advisory followed due to demonstrated effects of Hg and PCB exposure on the health of the fetus and newborns. This advisory focused on adults and most specifically on young and pregnant women. In 2008, the Faroese health authority concluded that pilot whales currently exceed limits for acceptable concentrations of toxic ontaminants and can no longer be recommended for human consumption. In the case of the Faroe Islands, the risk communication efforts appears to have been successful in convincing pregnant women to consume less pilot whale than before. While Hg levels in pilot whales have not decreased over the last three decades, concentrations in the blood of pregnant women have decreased significantly. While a dietary shift can be caused by several factors, it is likely that the risk communication undertaken in the Faroe Islands was the driving force for the decreases in human tissue levels of Hg and PCB for several reasons. For example, associated with the extensive cohort studies that have been ongoing since 1985, risk communication was continuous throughout the years and reached all areas of the islands. Further, risk communication messages were always restricted to pilot whale consumption, and several fish species with low contaminant concentrations were available and recommended as alternative dietary choices. However, health effects are still measurable even at these falling levels of exposure. Additionally, the success of the risk communication efforts and lower levels of contaminants in the Faroese population comes at a cost of loss of cultural identity for the Faroese people, who have relied on pilot whales as a staple part of their diet for hundreds of years.

WO-061

IMPACT OF NARRATIVE MESSAGES ON REDUCING FISH-RELATED CONSUMPTION OF MERCURY AMONG WOMEN OF CHILDBEARING AGE

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Many women of childbearing age (WCBA) avoid eating fish due to concerns about mercury exposure, and therefore miss out on the benefits of fish consumption for themselves and their potential offspring. To increase consumption of fish low in mercury, we tested the impact of a short brochure using a personal narrative (messages communicated as part of a story about a hypothetical woman of childbearing age) to supplement traditional risk/benefit information about fish consumption among licensed WCBA anglers in the Great Lakes coastal region of the US. We conducted a randomized, two-wave longitudinal experiment, involving 1,135 WCBA drawn from a sample of licensed anglers, between May 18th, 2014 and September 5th, 2015. Participants reported their fish consumption in summer 2014 by completing an online diary for relevant meals. We then randomly assigned women to three groups for spring 2015: no-exposure control; sent brochure with a short personal narrative; sent brochure with no narrative. All WCBA participants completed a fish consumption diary again in summer 2015. Women who ate the least fish (< 0.7 meals/week at baseline) stood to benefit the most from increasing their fish consumption. Among these women who confirmed that they saw the brochure, those who were exposed to the brochure that included the narrative ate more fish the next year. These women increased their fish consumption largely by eating more low-mercury, purchased fish. These women did not increase their consumption of more contaminated fish. We also found that women who ate too much fish (>2.8 meals/week at baseline) were also influenced by the narrative form of the brochure.

They ate fewer meals after receiving the brochure, but did not decrease their consumption sufficiently to be within advisory recommendations. It is not known how these changes impacted mercury ingestion. In the next stage of our analysis we will estimate actual mercury ingestion by linking data from womens diaries with available data on the mercury levels in different types of fish. We will use ordinary least squares regression to test the effect of the brochures on changes in ingested mercury. The results will be useful for government agencies responsible for communicating the benefits and risks of fish consumption.

WO-062

DO BELIEFS ABOUT SEAFOOD CONSUMPTION CORRELATE WITH FISH CONSUMPTION BEHAVIORS AMONG ASIANS IN CHICAGO?

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BACKGROUND: Asians have higher methyl mercury (MeHg) levels compared to other U.S. racial/ethnic groups due to frequent seafood (fish and shellfish) consumption. There is little information about how seafood consumption attitudes and knowledge among Asians contribute to their consumption behavior. The aim of this analysis is to assess how beliefs about seafood consumption, as well as other social-demographic characteristics, impact seafood consumption behavior among three Asian ethnic groups in Chicago, using preliminary data from the Fish Intervention for Health (FISH) study.

METHOD: Fish consumption and social-demographic data were collected through in-person interviews from Chinese, Korean and Vietnamese adults who consumed seafood at least monthly. Social-demographic characteristics include age, sex, BMI, income, ethnicity, marital status, English proficiency and years in the US. We elicited awareness about benefits and risks of seafood consumption using open ended questions, and responses were classified into seventeen components. Logistic regression was used to examine the associations of knowledge about fish consumption risks and benefits with seafood consumption frequency, adjusting for covariates.

RESULTS: A total of 275 participants were included in this analysis, of which 229 (83.3%) were women. The mean age of the participants was 44.2 years old (range from 18 to 80). Eighty-nine (32.4%), 61 (22.1%) and 125 (45.5%) participants were Korean, Vietnamese and Chinese respectively. Of the 275 participants, 123 (44.7%) reported eating seafood at least 3 times/week, 128 (46.7%) 1-2 times/week and 24 (8.6%) 1-3 times/month. The most commonly reported known benefit about seafood consumption was that seafood is low in fat (36.4%) and the least reported was that seafood is good for breast feeding (1.5%). The most commonly reported risk about seafood consumption was elevated Hg in fish(30.2%) and the least reported risk was to avoid certain fish parts (1.5%). Among social-demographic characteristics, Korean ethnicity (OR: 3.3; 95%CI: 1.6-7.1; P=0.02) and receiving food stamps (OR: 0.5; 95%CI: 0.3-0.9; P=0.04) were associated significantly with seafood consumption frequency. Of the risks and benefits factors, only fish is good for the heart was associated significantly with increased seafood consumption (OR: 1.8; 95%CI: 0.9-3..7; P=0.09) at P level less than 0.1.

CONCLUSION: Knowledge about the benefits and risks of seafood consumption among study participants varied and did not influence seafood consumption behavior. Interventions to increase the awareness of the seafood advisories to lower Hg and PCB exposure while maintaining or improving consumption of omega-3 FAs from seafood are warranted in this study population.

WO-063

THE ROLE OF THE PHYSICIAN AS A COMMUNICATOR ON FISH CONSUMPTION

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Multiple studies have shown that physicians continue to be the most trusted source of health information, even with easy access to information on the internet. Physicians in the US receive little instruction on environmental health and specifically on the health benefits and risks of fish consumption. A 2011 survey of 2,625 obstetricians found that less than 25% take an environmental health history from their patients. The fish consumption message is complex since advice includes information on frequency of consumption as well as specific species to avoid and others to recommend. Methods to increase the capacity of physicians to incorporate environmental health into their clinical practices include offering courses for Continuing Medical Education credits, providing them with environmental screening forms, adding screening questions to the electronic health record, and including environmental health questions on the specialty board certification exams. In this presentation I will cover my recent efforts to increase physicians capacity to advise patients about healthy fish consumption. With funding from the Great Lakes National Program Office at USEPA, my team developed the Healthy Fish Choices on-line curriculum for healthcare providers that uses adult learning modalities to promote change in clinical practice to include advise on fish consumption. Of 105 providers from the Great Lakes states who evaluated the curriculum immediately after completing the modules, 89.2% stated that they would implement modifications in their clinical practice. Six months later, 79.1% had adopted new practices to enhance their care regarding fish consumption. With short patient visits and increased demands to address disease prevention as well as treatment, succinct screening questions can help physicians determine risk quickly and therefore indicate which patients need further testing or messaging. I will present results from a project in which we are testing a fish consumption screening question to predict elevated blood mercury in prenatal patients. These findings will inform interventions aimed at busy clinicians who dont have time for extensive risk assessments in everyday practice. Finally, I will describe the efforts of the EPA/ATSDRfunded Pediatric Environmental Health Specialty Units (PEHSUs) to reach out to prenatal providers and to function as expert consultants in reproductive environmental health in their federal regions. In the last three years each PEHSU has added a reproductive healthcare provider to its unit. These midwives and obstetricians are working to increase their own knowledge and expertise in reproductive environmental health while providing a much-needed link to their colleagues and professional organizations.

WO-064

INFORMING PREGNANT WOMEN ABOUT THE BENEFITS AND RISKS OF EATING FISH

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Humans exposed to methylmercury (MeHg) can suffer from adverse neurological impacts, and because eating fish is the primary mechanism of MeHg exposure, federal and state agencies issue fish consumption advisories (FCAs) to inform the public about the risks of eating contaminated fish. However, fish is also a good source of omega-3s which promotes infants neurological development. Health care providers (HCPs) provide similar information to their pregnant patients. The information from FCAs and HCPs enable pregnant women to make better food choices; however, the difficulty in communicating both the risks and benefits of eating fish can lead to over-restricted fish consumption.

To measure the effectiveness of Maines FCAs, we conducted a survey to assess the awareness of the advisory and measure advisory-induced changes in (1) knowledge of the risks and benefits of eating fish, (2) knowledge of the benefits of omega-3 fish oil consumption and (3) species-specific fish consumption behavior. We focus on examining differences between readers and non-readers of the advisory. We find the FCA successfully increased womens knowledge of both the benefits and risks of consuming fish. It also increased their: ability to differentiate fish by their MeHg content, knowledge of both low and high-MeHg fish and knowledge of detailed attributes of seemingly substitutable goods, such as white and light tuna. Non-readers could not identify fish that provide: health benefits like Omega-3 fatty acids or health risks like MeHg. Readers increased ability to make substitutions to minimize risk while maintaining the benefits of eating fish suggests the advisory may reduce MeHg-related health risks while avoiding the drop in fish consumption show in other studies.

Since HCPs are an important source of food information for pregnant women, we were interested in learning about their knowledge and perception of important food safety and nutrition topics. We used data from a national survey of OBGYNs, nurse practitioners, nurse midwifes, physician assistants, and WIC educators to examine the perceptions held by HCPs regarding their role to provide fish consumption advice during pregnancy. We found HCPs are not systematically providing all recommended advice about each of these topics to their pregnant patients. Rather, within each category HCPs are more likely to supply some advice over others. These findings suggest that, especially in multi-provider practices, clarifying the role of providing food safety and nutrition information to patients is important.

4c: Anthropogenic emissions: Monitoring and analysis to support mitigation

WO-065

CURRENT AND FUTURE LEVELS OF MERCURY EMISSION ON GLOBAL SCALE: QUANTITATIVE ASSESSMENT AND ANALYSIS OF MITIGATION OPTIONS

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An assessment of current and future emissions of mercury worldwide is presented on the basis of results obtained during the duration of the EU GMOS (Global Mercury Observation System) project. Emission estimates for mercury were prepared with the main goal of applying them in models to assess recent (2013) and future (2035) air concentrations, and atmospheric deposition trends of this contaminant. In this way, the project contributed to monitoring the implementation of international agreements on mercury emission reductions and its impacts on environmental and human health.

The combustion of fossil fuels (mainly coal) for energy and heat production in power plants and in industrial and residential boilers, as well as artisanal and small-scale gold mining, are the major anthropogenic sources of mercury emissions to the atmosphere at present. These sources account for between 37% and 25% of total anthropogenic mercury emissions globally, estimated to be about 2000 t. Emissions in Asian countries, particularly in China and India, dominate the total emissions. The current estimates of mercury emissions from natural processes (primary mercury emissions and re-emissions), including mercury depletion events, were estimated to be 5207 t annually, which represents nearly 70% of the global mercury emission budget. Oceans are the most important source (36 %), followed by biomass burning (9 %). A comparison of the 2035 anthropogenic emissions estimated for three different scenarios with current anthropogenic emissions indicates a reduction of these emissions in 2035 of up to 85% for the best-case scenario.

Two global chemical transport models have been used within the

GMOS project for the evaluation of future mercury pollution levels considering future emission scenarios. Projections of future changes in mercury deposition on a global scale simulated by these models for three anthropogenic emissions scenarios of 2035 indicate a deposition decrease of up to 50% in the Northern Hemisphere, and up to 35% in Southern Hemisphere for the best-case scenario.

A discussion on mitigation measures that need to be employed in order to achieve the 2035 emission reduction targets is also presented

WO-066

FUTURE PERSPECTIVE AND MITIGATION OPTIONS FOR ATMOSPHERIC MERCURY EMISSIONS IN CHINA

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We have presented atmospheric Hg emissions in China for the year 2020 and 2030 in this study. We find that atmospheric Hg emissions are projected to be similar as the emissions in 2010 (approximately 539 t) under business as usual scenario. This indicates that the Hg removal by the progressive end-of-pipe pollution control measures will be offset by the Hg input from increased energy consumption and products production. By using the stringent control technologies, atmospheric Hg emissions can be reduced by up to 76.9% in 2030 at the accelerated pollution control technology scenario. Future emission scenarios imply different mitigation options for the convention-regulated sectors. Current legislations and progressive pollution control (eg., dust collection, desulfurization and denitration measures) will be the primary mitigation options for controlling emissions from coal-fired power plants, coal-fired industrial boilers, and nonferrous metal smelting, which will reduce 87%, 55% and 74% of current emissions (compare to 2010), respectively. Large-scale deployment of dedicated Hg removal technologies (eg., activated carbon injection and Boliden-Norzink technology) will aid to additional 2%, 35% and 15% of Hg reductions in these three sectors, respectively. For cement production, unless the stringent control measures (eg., dust shuttling) are fully applied, Hg emissions will increase by up to 22% in 2030 under the business as usual scenario. For municipal solid wastes incineration sectors, due to the sharp increase of incinerated solid wastes, Hg emissions will increase to 5.7-11.7 t in 2030, all larger than the emissions of 0.7 t in 2010. Thus, stringent control measures should be used in this sector.

WO-067

PARTICLE-BOUND MERCURY (PBM) AND ITS ASSOCIATION WITH CHEMICAL AND ISOTOPIC COMPOSITIONS OF PM2.5 IN KOREA: LOCAL URBAN ACTIVITIES AND REGIONAL-SCALE TRANSPORT OF MERCURY

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Due to rapid industrialization and urbanization in East Asia, the frequent occurrence of haze or smog is a growing concern. Particulate matter (PM), and especially, PM2.5, a transboundary atmospheric pollutant, is of particular interest as it has negative impacts on human health. Deciphering its origins and contributing sources is therefore vital for establishing effective reduction policies. We collected weekly PM2.5 samples from an urban (Seoul) and a rural (Baengnyeong Island) area in Korea from January 2014 to July 2016 and analyzed the isotopic compositions of PM2.5, including 13C, 15N, 34S- SO42-, 15N-NO3-, 18O-NO3-, and 15N-NH4+, as well as particle-bound mercury (PBM). The mean concentrations of PBM were 36 ± 34 pg m−3 at the Seoul site and 12 ± 11 pg m−3 on Baengnyeong Island. Obvious seasonal PBM variations were observed at both sites, as concentrations were higher in winter than in summer. At Baengnyeong, PBM concentrations showed good positive correlations with OC, EC, and Pb concentrations, as well as the isotopic compositions of 13C, 34S- SO42-, and 15N-NO3-, whereas 15N-NH4+ showed negative correlations with PBM. The stable isotopic compositions are expected to be more enriched with 13C, 34S-SO42-, and 15N-NO3- and depleted of 15N-NH4+ when PM2.5 arises from coal combustion rather than from vehicle and biogenic emissions. Thus, the positive correlations of 13C, 34S-SO42-, and 15N-NO3- with PBM and the negative correlations of 15N-NH4+ with PBM imply that the major PBM source during winter in Baengnyeong is coal combustion.

WO-068

AMBIENT ATMOSPHERIC MERCURY IN THE VICINITY OF TWO LARGE COAL FIRED POWER STATIONS AND OPEN CUT COAL MINES

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Measurement of ambient mercury concentrations has been undertaken over an extended period at a site in the Hunter Valley north of Sydney proximate to both coal fired power generation and mining activities. Mercury measurement at the site has been supplemented by measurements of SO2, particulates and meteorology. Results for more than 24 months of sampling have confirmed that mean annual ambient mercury levels are generally low by international comparison and in the range 0.8 -1.0 ng/m3. However, on occasion, higher level peaks of up to 2.5 ng/m3 and mercury depletion events have been observed. Some examples of these events and their possible causes are discussed. As the coal fired power stations are the only significant source of SO2 in the region, the contribution of this source to mercury concentrations can be determined by examining the relationship between SO2 and total gaseous mercury (TGM). However there is a poor correlation between high SO2 and TGM during the period suggesting that the power stations are not the source of the peak values of TGM. In fact SO2 rises sharply and falls rapidly again with elevated levels seldom extending beyond several hours, and mostly occurring from late morning to mid-afternoon under convective conditions when the plume from the stations reaches the ground. By contrast the high mercury concentrations appear to be associated with drainage flows following nocturnal inversion events; where low levels of atmospheric mixing enhanced by low wind speeds create stable conditions minimising dispersion and leading to the build up of higher levels of TGM trapped below the boundary layer height. The source of mercury emission for these events is the subject of on-going research.

WO-069

PARTICIPATORY MONITORING AND COMMUNITY PROTECTION FROM MERCURY POLLUTION GENERATED BY ARTISANAL GOLD MINING IN COLOMBIA

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After the abolition of slavery in 1851, Afro-communities inhabiting rural areas in the Pacific region of Colombia have depended on subsistence economies based on family farming, fishing, and traditional gold mining not involving the use of chemical reagents. Recently, the rise of international gold prices, the weakening of rural economies, and the lack of state control in rural areas has facilitated the migration of illegal gold miners into afrodescendant territories, and along with this, the use of mercury amalgamate to concentrate gold. Improper and irresponsible use of mercury in the illegal mines has led to devastating damages to the ecosystems on which the local livelihood depends, bringing a number of negative consequences for the neighboring communities. A first assessment of mercury levels in surface water was made in the District of La Toma, Cauca. Preliminary analysis with commercial strips show that aqueous levels of ionic mercury in the waterbody downstream of the illegal mines and the community drinking water are 50 to 1000 ppb, which is alarming. While institutional intervention hasnt been granted for controlling illegal mercury usage in the region, we aim to mitigate this problem by developing a citizen science program using low-cost portable sensors accessible to these communities for periodic monitoring of their water and food sources. For this, we have developed two nanosensors: 1) an electrochemical graphene-nanoplatinum electrode for analysis of methylmercury in fish tissue, and 2) a carbon nanodot photonic assay for analysis of ionic mercury in drinking water. The quantitative limit of detection in lake water for the two nanosensors was 11.1 ppb, and 12.5 ppb, respectively, and we are working to improve this as low as 1 ppb (4.5 nM). Both sensors have a response time of less than 5 min, and the range extends to 1000 ppb. These low-cost devices will be introduced in the community as analytical tools that will support an environmental monitoring and pollution control program run autonomously by community members. In addition to assessing the problem with nanosensors, high resolution spatiotemporal heat maps will be used to improve environmental risk models for rural communities of the Pacific region in Colombia. In the future, the nanosensor-risk model platform can be recreated in other regions of the world where mercury from mining is associated with social, environmental and public health problems.

WO-070

OPERATIONAL ACTIVITIES FOR THE REMEDIATION PROCESS IN THE FORMER HG MINING AREA OF ABBADIA SAN SALVATORE (SIENA, TUSCANY REGION, CENTRAL ITALY): AN UPDATE

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A reclamation program in the abandoned Hg world-class mining district of Abbadia San Salvatore (Tuscany, central Italy), whose activity ceased in 1976, has started with a geochemical characterization of surface and ground waters, soil, air and mining structures. In 2008, the former owner (ENI Ltd. - AGIP Division) transferred properties and mining concessions to the Municipality of Abbadia San Salvatore that now is the responsible of the reclamation process. The mining activities ended up without any clean-up strategy. The metallurgical plants and tailings, with huge piles of calcines and roasting products where relevant amounts of metallic mercury are still present, were abandoned. Mine adits and shafts were closed, leaving flowing drainage tunnels and two unsealed chimneys to disperse a natural flow of CO2-rich gas discharge. This occurred without strict environmental regulations that became State laws in 1999. Recently, the mining areas were divided in 6 sub-areas (lots) in accordance with the local Environmental Protection Agency, on the basis of the type of operations to be performed for reclaiming the mining area. Lot 6 represents the most critical one, being the site where cinnabar was managed and roasted to produce liquid mercury after condensation processes. The other lots are characterized by workers and managers buildings and then, less affected by Hg contamination.

In this work, we present an update of the reclamation activities, providing new original data on the different geological and anthropogenic materials included in the former mining concession. Most these compartments are indeed affected by Hg concentrations that are well above the threshold concentration limits for mercury according to regulations issued by the Tuscany Region for recovering abandoned mining areas. Consequently, operational activities are presently going on to minimize the presence of mercury in the building materials and edifices (including the air), soils and terrains and surface and underground waters. Actions, criticalities and perspectives for the remediation process, which is focused on environmental restoration to achieve a historic museum and mining park, are highlighted.The results are useful to the workers who are going to operate in the mining areas during the operational activities of remediation.

WO-071

SOURCES AND TRANSPORT OF MERCURY IN RESPIRABLE SUSPENDED PARTICULATE MATTER AT A RURAL SITE IN NORTH INDIA

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Atmospheric mercury is a global concern because of its high toxicity, transboundary transport and its ability to biomagnify and bioaccumulate. It causes great harm to the human health, ecosystem and environment. It has been extensively studied in different parts of the world, but very few studies are available from India. Therefore, this study is an attempt to report mercury levels in Respirable Suspended Particulate Matter (PM10-Hg) and to identify its potential sources of contribution through backward trajectories at a rural site (Mahasar, Haryana) located ~130 km SW of New Delhi. In this study, we have also measured the seasonal variability of PM10-Hg. The study was carried out during December 2014 to June 2015. Mercury was determined using differential pulse anodic stripping voltammetry through standard addition methods. The mean (± standard deviation) concentrations of PM10-Hg during winter and summer seasons were 1.01 ± 0.3 ng/m3 and 0.32 ± 0.2 ng/m3 respectively. The higher concentrations of PM10-Hg were observed in winter, possibly due to increased emissions from the combustion sources, reduced mixing heights, transportation from other regions and less precipitation. At the study site, burning of biofuels such as wood and cow dung cake for cooking and heating purposes is increased many folds during winter as compared to summer. Lower concentrations of PM10-Hg during summer might be due to increased mixing heights as well as due to the scavenging effect as some light to heavy rain events were also observed during summer time sampling. In order to find out the contribution of mercury from other source regions and the transport pathways of air masses arriving at our observation site, five-days backward airmass trajectories at three heights (500m, 800m and 1000 m) above the ground level were calculated using HYSPLIT model of NOAA. The analysis of these trajectories revealed that during peak winters, air masses were coming from the south and south-east regions of India which have been reported as the hot spots of coal deposits and coal mining activities as well as burning of coal in industries and thermal power plants. Probably, due to this reason, PM10-Hg was higher during winters, apart from local source contributions. Backward trajectory analysis revealed that PM10-Hg concentrations were lower when the airmasses were arriving from western India, Arabian Sea and Middle-East regions. The interesting results of this study need further comprehensive monitoring of different forms of mercury too.

WO-072

LONG-TERM MONITORING OF ATMOSPHERIC MERCURY AT A COASTAL SITE IN THE NORTHERN GULF OF MEXICO

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Atmospheric mercury species, including gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM) and particulate bound mercury (PBM), trace pollutants (including ozone, SO2, CO, NO, NOY and black carbon), and meteorological parameters have been continuously monitored since 2007 at an Atmospheric Mercury Network (AMNet) site in Grand Bay, Mississippi. Average hourly mercury concentrations and standard deviations were 1.40±0.23 ng m-3 for GEM, 5.9±11.4 pg m-3 for GOM, and 5.0±10.8 pg m-3 for PBM. Diurnal variation of GEM shows a slight increase in GEM concentration during the morning, likely due to downward mixing of higher concentrations from the residual layer. Seasonal variation of GEM shows higher levels in winter and spring. Diurnal variations of both GOM and PBM show peaks in the afternoon likely due to photochemical oxidation of GEM. Seasonally, PBM measurements exhibit higher levels in winter and spring and low levels in summer, while GOM measurements show high levels in early summer and late fall and low levels in winter. These data were analyzed using HYSPLIT back trajectories in order to develop source-receptor relationships for mercury species in this coastal environment. Trajectory frequency analysis shows that high mercury concentrations were generally associated with air masses arriving from areas with high mervery emissions, while low mercury levels were largely associated with trajectories passing through relatively clean areas. This study indicates that the receptor site, which is located in a coastal environment on the Gulf of Mexico, experienced impacts from mercury sources that are both local and regional in nature.

1c-1: Stable isotope studies of global mercury cycling and bioaccumulation

RO-001

A FULLY-COUPLED GLOBAL HG ISOTOPE BOX MODEL

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The large magnitudes of mass-dependent (MDF) and mass-independent fractionation (MIF) of stable Hg isotopes make it a useful tool to understand Hg biogeochemical cycling on Earth. Accurate understanding of the Hg isotope signatures in various Earth's reservoirs at a global scale needs to account for all the underlying Hg sources (primary natural/anthropogenic Hg emissions and re-emissions of legacy Hg) and biogeochemical processes that potentially fractionate Hg isotopes.

We integrate source Hg isotope MDF and MIF signatures and processes-based isotope fractionation factors (e.g., Hg0 exchange at the atmosphere-terrestrial and atmosphere-oceanic boundary layers, aqueous dissolved HgII reduction, elemental Hg0 oxidation, sorption of aqueous HgII onto particles) into a fully-coupled, global terrestrial-atmospheric-oceanic Hg isotope box model. The model is used to simulate three isotope signatures: δ202Hg (MDF), Δ199Hg (odd Hg isotope MIF) and Δ200Hg (even Hg isotope MIF). We find that the simulated Hg isotope compositions in the Earth's reservoirs using the best-available parameters are highly biased relative to several lines of observational constrains.

A series of sensitivity analysis suggests that MDF during atmospheric Hg0 oxidation enrich heavy Hg isotopes in the Hg0, in contrary to the sign indicated by experimental atmospheric Hg0 oxidation by Br atom. A similar MDF sign is also necessary for dissolved Hg0 oxidation in the ocean. To best fit the simulated results to the observational constrains, it requires anthropogenic Hg emissions to have lower δ202Hg than currently thought and a 2 times larger MDF factor for the Hg0 oxidation. Likewise, appropriate odd Hg isotope MIF factors for oxidation of Hg0 are also needed to reasonably simulate the observed Δ199Hg variation in the Earth's surface reservoirs. We find that an increase of the terrestrial Hg0 re-emission fluxes and associated odd MIF factors gives a closer agreement between model results and observational constrains.

RO-002

THE MYSTERIOUS MASS-INDEPENDENT FRACTIONATION OF EVEN MERCURY ISOTOPES

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Preliminary studies have demonstrated both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) of Hg isotopes in natural samples, and the potential of Hg isotope determination in biochemistry and geochemistry[1, 2]. To date, more than 100 papers have been published on Hg isotope ratios, which demonstrated the potential of Hg isotopes in tracing the source, processes and the fate of Hg in the atmosphere, biosphere, lithosphere, and hydrosphere. A few special processes such as photochemical reduction of Hg(II) and photochemical degradation of methylmercury (MeHg) can produce mass-independent fractionation (MIF) of odd Hg isotopes (odd-MIF), which had been largely reported in variable natural samples and laboratory experiments, and was thought to be caused by either nuclear volume effect (NVE) or magnetic isotope effect (MIE). Moreover, recent work reported, unexpectively, intriguing MIF of even Hg isotopes (even-MIF, D200Hg up to 1.24‰) in natural samples mainly related to the atmosphere, rendering Hg as a "three dimentional" isotope tracing system.

Here, we try to give a tentative review of publications on even Hg isotope anomalies, with a main focus on sample strategies and possible processes and mechanisms triggering even-MIF. Given the fact that even isotope anomaly was observed in variable regions with different altitude and latitude in China and in North America, the occurrence of even-MIF is likely a worldwide phenomenon, supported by the positive D200Hg (~ +0.22‰) determined in the tree moss in Sweden. In fact, D200Hg is actually used to refer to the deviation of even Hg isotopes from MDF, whether other even isotopes are subject to the same fractionation remains unclear and needs to be fully elucidated. In general, D200Hg values were mainly determined in samples related to the atmosphere, implying an upper atmosphere origin of even-MIF. If our conceptual model[3] can hold, even-MIF may serve as a useful indicator of upper atmosphere chemistry. The implication of even-MIF as a possible conservative tracer remains to be largely developed. In fact, 200Hg anomaly is likely related to solar irradiation, air mass move and stratosphere incursion, thus even-MIF could provide additional information about atmospheric chemistry, meteorological condition and even related climate changes. Moreover, the conservative behavior of 200Hg anomaly may also be helpful for better understanding the global biogeochemical cycle of Hg, especially the surface-atmosphere exchange.

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RO-003

ISOTOPIC FRACTIONATION OF HG DURING GAS-PHASE OXIDATION CAUSED BY CL•, BR•, HO•, O3 AND PHOTO-EXCITATION IN AIR

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In this study, we investigated the Hg isotope composition and fractionation during gas-phase oxidation of Hg0 by oxidants considered important in the atmosphere and incorporated in most current chemical Hg transport models (Br•, HO• and O3). In addition, the systems of Hg + Cl• and Hg + hν (UV-C radiation incl. λ=253.7 nm) + O2 (air) were also studied. The importance of former reaction falls within combustion processes and the latter reaction potentially has importance in the upper atmosphere.

Reaction kinetics of Hg0 oxidation by Cl•, Br•, HO• and O3 in air at atmospheric pressure (750±1 Torr) and room temperature (298±1 K) were determined by competitive and absolute kinetic techniques respectively to (1.8±0.5) × 10-11, (1.6±0.8) × 10-12, (2.7±1.89) × 10-12 and (4.6±0.5) × 10-20 cm3 molecule-1 s-1. Significant mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) were observed in all of the reactions studied. Results show that heavier isotopes are preferentially enriched in the remaining Hg0 during Cl•, O3 and UV-C initiated oxidation, whereas being enriched in the Hg(II) products during oxidation by Br• and HO•. Odd-mass-number MIF (Δ199Hg and Δ201Hg) is without exception positive for the reactant Hg0 and negative for the reactant Hg (II) pool, although of various magnitude for the specific oxidants falling in the order (Cl• > Br• > HO• > O3). Hg + UV-C light + O2 induces a large magnitude of even-mass-number MIF (Δ200Hg down to -39.9‰ in the remaining Hg0). This result has similarities to Hg fractionation pattern previous observed to occur in compact fluorescent lamps and will be further elaborated. Finally, the atmospheric relevance of Hg0 gas-phase oxidation will be discussed in connection to field observations of Hg stable isotope systematics.

RO-004

HISTORIC CHANGE IN MERCURY SOURCES AND CYCLING RECONSTRUCTED FROM ISOTOPIC RECORDS IN A GLOBALLY DISTRIBUTED SUITE OF LAKE SEDIMENT CORES

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The strongest evidence for anthropogenic alteration of the global mercury (Hg) cycle comes from historic records of mercury deposition preserved principally in lake sediments. More recently, high-precision measurement of Hg isotopes has added a new dimension to these sedimentary archives, promising additional insights into Hg source apportionment and cycling. At present, interpretations are constrained by the small number and geographic extent of cores analyzed isotopically. Here we report on newly acquired Hg-isotopic records from a globally distributed suite of well-dated sediment cores taken from remote lakes in the US (Alaska, Minnesota, California), Canada (Newfoundland), Kenya, and China. Most of these cores were analyzed previously for total-Hg and all show the global rise in Hg deposition associated with the industrial revolution. In nearly all cases, this rise is accompanied by an increase in mass dependent fractionation (MDF, reported in δ notation) and a decrease in mass independent fractionation (MIF, reported in Δ notation) of Hg isotopes. These trends, also noted in previous core studies, are attributed to large scale industrial emission of Hg (with little MIF) into the global atmosphere and are consistent with positive MDF and MIF as measured in modern-day precipitation. Most cores show negative MIF in preindustrial sediments, indicating Hg sources (e.g. organic soils) that have undergone significant recycling, including photochemical reactions that generate MIF. However, other cores show positive MIF in preindustrial times, suggesting that direct atmospheric deposition could be an important Hg source for some lakes, especially those with relatively small watersheds. Despite similar temporal trends among cores, the actual isotopic signatures vary considerably among the different study regions, with some cores showing highly negative MIF (e.g., southeastern Alaska; Δ199Hg = -0.2 to -0.4 per mil) and others highly negative MDF (e.g., northwestern China; δ202Hg = -3 to -5 per mil) throughout the period of record. Such differences may reflect Hg source differences, as well as fractionation effects during atmospheric transport and deposition, and during Hg cycling in the water column (e.g., Hg residence time, sedimentation rate, water clarity). Differences among the study lakes in latitude, precipitation source region, relative watershed size, and distance from Hg emission sources provide an empirical framework for evaluating Hg isotopic signatures and global Hg cycling in recent centuries.

RO-005

EFFECTS OF CHINESE INDUSTRIALIZATION AND ECONOMIC GROWTH ON MERCURY INPUTS TO MARGINAL SEA SEDIMENTS: INSIGHTS FROM MERCURY STABLE ISOTOPES

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Economic development in the past few decades has made China the largest user and emitter of Hg in the world, however, the effect of such economic development on Hg inputs to the nearby oceans is still unclear. In this study, the influx and isotopic composition of Hg in four

210Pb-dated sediment cores was examined to investigate changes in Hg deposition to major marginal seas in China. Our results show a clear increase in Hg influx since the 1950s, during which time China started its First National Five-Year Plan for economic development. Mercury influxes have increased rapidly since the late 1970s, which coincides with the launching of China's Economic Reform policy. Increased input of industrial Hg is causative for the observed Hg influx increases. Both mass dependent fractionation (MDF) and mass independent fractionation (MIF) of Hg isotopes were observed. Values of δ202Hg in all cores have shifted following the 1950s, and δ202Hg has increased dramatically (-2.0 to -0.7‰). Offshore cores show small but significantly positive MIF signatures (Δ199Hg: 0.1 to 0.3‰), whereas open ocean cores mainly show slightly negative MIF signals (Δ199Hg:-0.2 to 0‰). Negative MIF in the deep layers of coastal cores suggest input by soil Hg; however, open ocean cores exhibit positive MIF, attributed to atmospheric deposition. Uppermost portions of the cores had lower MIF signals than deep sediments, which can be explained by the dilution of industrial Hg. Historical Hg influxes of industrial, watershed, and atmospheric Hg were calculated a triple-mixing isotope model. According to the model output, increases in industrial Hg began in the 1950s and accelerated in the 1970s, in accordance with increases in industrial Hg inputs due to the economic development of China. Interestingly, decreases in watershed Hg influx were observed since the 1960s, and this decline may be attributed to intense dam construction, enhanced water-soil conservation, and increased water consumption during this period.

RO-006

STABLE ISOTOPIC EVIDENCE FOR MERCURY ACCUMULATION IN THE MONTANE FORESTS IN SOUTHWEST CHINA

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Mercury (Hg) accumulation in montane forested areas plays an important role in global Hg cycling. In China, montane forests account for about 90% forested areas, 25% of which located in Southwest China. In this study, we characterized stable Hg isotopic composition at the background forest sites of Mt. Ailao, Mt. Leigong, Mt. Gongga, and 23 forests in Tibetan Plateau. We aimed to identify Hg isotope fractionation caused by the translocation of atmospheric Hg to the forest floor. Similar isotope compositions were observed in foliage of different tree species. At Mt. Ailao, the Hg isotope signature of bulk leaf sprout samples (δ202Hg = 0.08±0.74‰, Δ199Hg = −0.20±0.14‰) was similar to those of gaseous air samples (δ202Hg= 0.37±0.44‰, Δ199Hg = −0.18±0.04‰) suggesting that atmospheric Hg0 is a major source of Hg found in foliage. Negative δ202Hg-shift (3‰) and Δ199Hg-shift (0.10-0.15‰) were observed during the growing season. Hg0 effluxes from mature foliage exhibits a large, positive mass independent fractionation (MIF) signature (Δ199Hg = 0.17±0.40‰) in contrast to ambient air and leaf samples. During a 2-year litter decomposition period, δ202Hg, Δ199Hg and Hg mass varied slightly, suggesting a steady Hg accumulation in decomposing litter biomass. In contrast to those observed in fully decomposed litter (Oa soil) and 0-5 cm mineral soils, positive δ202Hg-shift (0.5-1‰) was observed, and 0-0.2‰ negative Δ199Hg-shift was dependent on the density of forest canopy. The negative Δ199Hg in the surface soil samples were comparable to the observed Δ199Hg in litter, but significantly different from the positive Δ199Hg in throughfall/rainfall at 26 forest sites. This suggests that Hg input from litter is a predominant source for Hg accumulation on high montane forest floor. Enhanced Hg accumulation and more negative MIF in soil was observed at higher elevations at Mt. Leigong while such altitudinal trends were not found at Mt. Ailao and the sites of Tibetan Plateau. Statistical analysis suggests that precipitation and temperature mediated litter biomass production plays an important role in Hg accumulation in forest ecosystems.

RO-007

PROVING THE FEASIBILITY OF PASSIVE SAMPLING FOR ISOTOPIC FINGERPRINTING OF ATMOSPHERIC MERCURY

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Plants play an important role in the biogeochemical cycle of mercury (Hg) in the environment. It is generally considered that roots act as a barrier to the translocation of soil Hg to aboveground tissues, thereby mitigating Hg stress. However, a critical question that remains to be answered is how Hg is assimilated and sequestered in root. To address this question, we collected Houttuynia cordata, a widely distributed plant in southern China, from Wuchuan Mercury Mine, SW China, and measured the isotopic composition of Hg using multi-collector-inductively coupled plasma mass spectrometry (MC-ICP-MS) and its chemical forms using high energy-resolution X-ray absorption near edge structure (HR-XANES) spectroscopy. Houttuynia cordata Thunb can be a potential accumulating plant of soil Hg due to its large root biomass and relatively high Hg concentration. The concentrations of Hg varied from 0.4 to 1.5 mg/kg DW in primary roots, and 2.3 to 16.0 mg/kg DW in secondary roots, and were similar to the Hg concentration in soils (0.2 to 5.2 mg/kg DW). Both mass dependent fractionation (MDF, denoted δ) and mass independent fractionation (MIF, denoted Δ) of Hg isotopes were observed in the plant-soil system. Significant differences in δ202Hg values were observed between soils (-2.3‰≤ δ202Hg ≤ -1.2‰ ±0.1‰) and roots (primary root:-5.1‰ ≤ δ202Hg ≤ -3.7‰ ±0.1‰; secondary root: -5.7 ‰≤ δ202Hg ≤ -3.2‰ ±0.1‰). Soil Hg had no MIF (-0.07‰ ≤ Δ199Hg ≤ 0.04‰ ±0.04‰), in contrast to primary (0.03‰

≤ Δ199Hg ≤ 0.11‰ ±0.04‰) and secondary roots (0.06‰ ≤ Δ199Hg ≤ 0.14‰ ±0.04‰). Although small, the differences of MIF between soil and roots were statistically significant ($P < 0.05$). The more negative δ202Hg values in roots relative to the soils suggest that MDF occurs during the transport and diffusion of Hg from the rhizosphere to the root interior. The positive MIF values in roots suggest that Hg may bind to thiol ligands. Complexation of Hg to thiol sulfur in the roots was demonstrated by HR-XANES, which showed that 82% to 100% (± 10%) of Hg was in Hg(SR)2 complex. Small amounts of nano-particulate β-HgS were detected in three root samples (up to 18 ± 10%). In soils, Hg was mainly present as α-HgS and nano-particulate β-HgS. The absence of α-HgS and paucity of nano-particulate β-HgS in roots and lack of detectable Hg(SR)2 in soils suggest that mercury uptake proceeds through the oxidation of mercury sulfide and subsequent solubilization of divalent mercury. The underlying molecular mechanisms leading to mercury release, transfer, and accumulation in roots can be accompanied by the fractionation of the Hg isotopes.

RO-008

UNDERSTANDING HG UPTAKE AND SEQUESTRATION IN THE ROOT OF HOUTTUYNIA CORDATA USING STABLE HG ISOTOPE TRACER AND HIGH ENERGY-RESOLUTION X-RAY ABSORPTION NEAR EDGE STRUCTURE SPECTROSCOPY

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Plants play an important role in the biogeochemical cycle of mercury (Hg) in the environment. It is generally considered that roots act as a barrier to the translocation of soil Hg to aboveground tissues, thereby mitigating Hg stress. However, a critical question that remains to be answered is how Hg is assimilated and sequestered in root. To address this question, we collected Houttuynia cordata, a widely distributed plant in southern China, from Wuchuan Mercury Mine, SW China, and measured the isotopic composition of Hg using multi-collector-inductively coupled plasma mass spectrometry (MC-ICP-MS) and its chemical forms using high energy-resolution X-ray absorption near edge structure (HR-XANES) spectroscopy. Houttuynia cordata Thunb can be a potential accumulating plant of soil Hg due to its large root biomass and relatively high Hg concentration. The concentrations of Hg varied from 0.4 to 1.5 mg/kg DW in primary roots, and 2.3 to 16.0 mg/kg DW in secondary roots, and were similar to the Hg concentration in soils (0.2 to 5.2 mg/kg DW). Both mass dependent fractionation (MDF, denoted) and mass independent fractionation (MIF, denoted) of Hg isotopes were observed in the plant-soil system. Significant differences in 202Hg values were observed between soils (-2.3 202Hg -1.2 0.1) and roots (primary root:-5.1 202Hg -3.7 0.1; secondary root: -5.7 202Hg -3.2 0.1). Soil Hg had no MIF (-0.07 199Hg 0.04 0.04), in contrast to primary (0.03 199Hg 0.11 0.04) and secondary roots (0.06 199Hg 0.14 0.04). Although small, the differences of MIF between soil and roots were statistically significant ($P < 0.05$). The more negative 202Hg values in roots relative to the soils suggest that MDF occurs during the transport and diffusion of Hg from the rhizosphere to the root interior. The positive MIF values in roots suggest that Hg may bind to thiol ligands. Complexation of Hg to thiol sulfur in the roots was demonstrated by HR-XANES, which showed that 82% to 100% (10%) of Hg was in Hg(SR)2 complex. Small amounts of nano-particulate -HgS were detected in three root samples (up to 18 10%). In soils, Hg was mainly present as -HgS and nano-particulate -HgS. The absence of -HgS and paucity of nano-particulate -HgS in roots and lack of detectable Hg(SR)2 in soils suggest that mercury uptake proceeds through the oxidation of mercury sulfide and subsequent solubilization of divalent mercury. The underlying molecular mechanisms leading to mercury release, transfer, and accumulation in roots can be accompanied by the fractionation of the Hg isotopes.

1d-1: Mercury cycling, bioaccumulation and health impacts in polar regions

RO-009

A REVISED RIVER HG FLUX TO THE ARCTIC OCEAN

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Elevated mercury (Hg) levels in Arctic marine biota have long been associated with atmospheric transport and deposition of anthropogenic Hg emissions from the mid-latitudes. Recent modeling studies suggest that Arctic river inputs have been a potentially overlooked source of Hg to the Arctic Ocean. Observations on Arctic river Hg fluxes, in particular from Eurasian rivers, are scarce however. Here we present seasonal observations on dissolved (DHg) and particulate Hg (PHg) concentrations and fluxes for two large Eurasian rivers, the Yenisei and the Severnaya Dvina. We observe large DHg and PHg fluxes during the spring freshet, followed by a smaller, second pulse during the fall. We compare water discharge, watershed area and Hg export relationships for Eurasian and North-American rivers. Using additional Hg freshet observations for the Great Whale river (Hudson Bay), we are able to define run-off vs Hg yield relationships for Eurasian and N-American Hg fluxes to the Arctic Ocean and for Canadian Hg fluxes into the larger Hudson Bay area. By extrapolating these DHg and PHg relationships to pan-Arctic rivers and watersheds we estimate total Hg fluxes to the Arctic Ocean of 31 Mg y-1 which is on the lower end of model-based estimates of 16-80 Mg y-1 and Hg/DOC ratio extrapolated estimates of 50-108 Mg y-1.

RO-010

A MASS BALANCE OF ATMOSPHERIC MERCURY DEPOSITION IN THE ARCTIC TUNDRA: GASEOUS ELEMENTAL MERCURY UPTAKE DRIVES A GLOBALLY-IMPORTANT MERCURY SINK

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To assess atmospheric Hg inputs to the vast circumpolar tundra biome – covering 6% of the global land surface area –we developed a mass balance of atmospheric Hg deposition in the continental Arctic at Toolik field station in northern Alaska, USA (68°38'N, 149°36'W). Over two years, we correspondingly measured net gaseous elemental Hg0 deposition using micrometeorological techniques, deposition of wet HgII and dry HgII, and vegetation Hg inputs. We also conducted detailed Hg stable isotope measurements in the atmosphere, snowpack, vegetation, and soils to quantify sources, and performed atmosphere-snow-soil Hg0 concentration profiles to determine zones and underlying processes that drive atmospheric Hg0 sources and sinks.

We observed that gaseous Hg0 deposition of 6.5±0.7 µg m-2 yr-1 accounted for 71% of total deposition over the two years of measurement. Wet HgII deposition was 30 times lower (0.2 ± 0.1 µg m-2 yr-1) and dry deposition of HgII was 2.5 µg m-2 yr-1 (range 0.8 to 2.8 µg m-2 yr-1). Gaseous Hg0 deposition was driven by a Hg0 wintertime uptake and was enhanced in summertime due to vegetation uptake of Hg0. No photochemical re-emission of Hg0 from the snowpack is observed during the snow-covered period aside from surface re-emissions during springtime during mercury depletion events. Therefore, we conclude that during most of the year re-volatilization of Hg0 is not an important process in the Arctic tundra and that repeated deposition-emission cycles occurring at lower latitudes are tilted toward net Hg0 deposition. Deposition of gaseous Hg0, along with old soil age, explains high Hg loads in tundra soils which exceed levels at temperate sites several-fold, and explains the conundrum that watersheds with some of the lowest Hg wet deposition loads on Earth and limited impacts from AMDEs show elevated Hg in riverine runoff. Our measurements suggest that the Arctic tundra is a globally important sink for atmospheric Hg0 storing up to half of the world's soil Hg. Anthropogenic climate change represents a risk for re-mobilization of massive tundra soil Hg.

RO-011

MERCURY CYCLING IN A SUB-ARCTIC MIRE: INSIGHTS FROM STORDALEN, ABISKO

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Permafrost thaw driven by climate change in northern high latitudes is thought to play a significant role in enhancing the mobilization of previously sequestered peatland mercury (Hg) to the atmosphere and hydrosphere. Though studies have shown sub-arctic Hg dynamics to be impacted by adjacent permafrost thaw, the magnitude and long-term effects of Hg mobilization in this climate-sensitive ecosystem remain poorly constrained.

To investigate the coupling of different export pathways of Hg, along with the effects on Hg cycling resulting from the evolution of this mire as climate change reshapes the landscape to more fully thawed zones, we measured total gaseous Hg (TGM) fluxes across a permafrost thaw gradient and compared these fluxes to the total Hg measured in peat and lake sediment cores collected at the Stordalen Mire, Abisko, Sweden (68°21'N). In two of the peat core sites we also measured pore water methyl mercury (MeHg) contents.

Mercury flux measurements were estimated using a Tekran 2537 ambient air mercury analyzer integrated into a dynamic chamber system. The nine chamber array is divided into three sites, three chambers per site: (1) Palsa: dwarf-shrub dominated hummocks overlying permafrost, (2) Sphagnum: semi-wet hollows with 100% sphagnum cover with minor Eriophorum vaginatum, and (3) Fen: wet hollows dominated by Carex rostrata and Eriophorum angustifolium. All three sites show variability in the relative magnitude of deposition/evasion throughout the day but consistently show a diel pattern characterized by Hg deposition during lows of photosynthetically active radiation (PAR) and ground temperature and a release of Hg during peak PAR hours and ground temperature periods (13:00-15:00h).

Consideration of the Hg flux measurements along with total Hg concentrations of the peat suggests that palsa has the highest amount of stored Hg. The Sphagnum- dominated sites have less abundant Hg in the core (1-20 ng/g) than the palsa (10-60 ng/g), and the fen sites have intermediate values (1-70 ng/g), at certain depths comparable to the peat cored from the palsa. All core profiles have the highest total Hg concentrations near the surface and decrease with depth. The fen site contains elevated Hg near the surface relative to the Sphagnum while also containing significantly higher levels of pore water MeHg.

Taken together our results suggest that during initial stages of permafrost thaw export of gas-phase mercury may be an important pathway, but as thawing continues mercury export into the hydrosphere becomes significant and environmental conditions for MeHg become more favorable.

RO-012

MERCURY EXPORTS FROM CONTRASTING LOW AND HIGH ARCTIC WATERSHEDS IN CANADA

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Climate change is rapidly altering the Arctic's freshwater cycle. Glaciers and ice sheets are melting, permafrost is thawing and precipitation is increasing throughout the north. In fact, conservative climate models predict that in 50 years, river discharges to the Arctic Ocean may increase by 25-50% with yet unknown consequences on water quality, productivity and physical structure of nearshore marine environments. Our ability to predict the future health and productivity of these marine arctic ecosystems thus ultimately depends on our understanding of arctic freshwater resources discharging to them. Here we present the results of detailed water quality surveys of two arctic watersheds in northern Canada: one in the High Arctic dominated by glacier melt, and one in the Low Arctic defined by extensive retrogressive thaw slump activity. The Lake Hazen watershed (82°N) is anchored by Lake Hazen (544 km2, 267 m deep), which collects meltwater from the Grant Land Ice Cap before discharging into the Ruggles River and then Chandler Fjord and Nares Strait between northern Ellesmere Island and Greenland. The Peel River watershed (68°N) is a tributary of the Mackenzie River, a major inflow to the Beaufort Sea. Transects extending from glaciers/permafrost slumps downstream were completed in 2015 and 2016 to assess the impacts of changes in the terrestrial cryosphere to mercury exports from catchments. In the Lake Hazen watershed, average total mercury (THg) and methylmercury (MeHg) concentrations in 7 glacial rivers were 9.7 and 0.048 ng L-1, respectively. High density turbidity currents transported these waters to the bottom of Lake Hazen, making this ultra-oligotrophic lake a sink for predominately particulate-bound Hg. Although Lake Hazen itself was not an important contributor of Hg to the Ruggles River, slump activity downstream of the lake increased THg and MeHg exports to the marine environment by an order of magnitude relative to the outflow of Lake Hazen. In the Peel Plateau, THg and MeHg concentrations, averaged over 8 slumps, increased from 4.5 and 0.296 ng L-1 upstream of the slumps to 296 and 1.68 ng L-1 downstream, with maximum THg and MeHg concentrations reaching 2.05 µg L-1 and 10.1 ng L-1. Flux estimates for each catchment will be presented. These results highlight the mobilization of mercury previously locked in various forms of ice to aquatic ecosystems with potential consequences for mercury cycling in downstream receiving systems.

RO-013

CHANGE IN LAKE SENSITIVITY TO METHYLMERCURY BIOACCUMULATION ACROSS A CANADIAN LATITUDINAL GRADIENT

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We investigated monomethylmercury (MMHg) bioaccumulation in lakes across a 30° latitudinal gradient in eastern Canada to test the hypothesis that climate-related environmental conditions affect the sensitivity of Arctic lakes to atmospheric mercury pollution. Aquatic invertebrates (chironomid larvae and bulk zooplankton) were used as indicators of MMHg bioaccumulation near the base of benthic and planktonic food chains. Previously published estimates of atmospheric mercury deposition in Canada showed this mercury flux declines with latitude. In step with that trend, we observed lower concentrations of THg in both water and sediment in higher latitude lakes. Despite latitudinal declines of inorganic mercury exposure, MMHg bioaccumulation in aquatic invertebrates did not concomitantly decline. The highest MMHg concentrations in zooplankton and chironomids were observed in sub-Arctic (55N) and polar desert lakes (75N). Lakes with greater MMHg in aquatic invertebrates either had higher water MMHg concentrations (reflecting ecosystem production of MMHg) or less MMHg in water but also low water concentrations of DOC, chlorophyll and total nitrogen (reflecting ecosystem sensitivity). The MMHg:DOC ratio of surface water was a highly significant explanatory variable that may be useful to predict lake sensitivity to mercury pollution. Bioaccumulation factors of basal organic matter sources (rock biofilms, seston) showed more efficient uptake of MMHg in low DOC lakes. Our findings demonstrate that Arctic lakes are more sensitive to mercury pollution and this sensitivity is related to the low amount of organic matter in their surface waters. Climate-related controls on lake productivity and DOC influence the fate of mercury deposition on a broad geographic scale.

RO-014

AIR-SEA EXCHANGE OF ELEMENTAL MERCURY OVER THE OPEN ARCTIC SEA

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Elemental mercury, Hg(0) is emitted to the atmosphere from natural and anthropogenic sources and deposited in the oceans as inorganic divalent Hg, Hg(II). Around 80% of the Hg(II) deposited into oceans has been estimated to be reduced and re-emitted to the atmosphere.

Oceans cover ~60% of the worlds surface and the re-emission of Hg(0) from sea surfaces is an important source of Hg to the atmosphere. The air-seawater flux of Hg(0) is commonly estimated using gas exchange models based on the calculated gas transfer velocity, the Henry´s law coefficient and the concentration gradient of Hg(0) between air and surface seawater. Geographical variations in the air-seawater flux of Hg(0), especially in areas partly covered with ice such as the arctic, is a major contributor to the uncertainty in current global Hg models.

During the SWEDARCTIC 2016 expedition (8th of August to 20th of September, 2016) in the Arctic Ocean arranged by the Swedish Polar Research Secretariat (SPRS), gaseous elemental mercury (GEM), dissolved gaseous mercury (DGM) in surface seawater and Hg(II) species in air were continuously measured. The expedition started and ended in the East Greenland Rift Basin crossing the Eurasian Basin, the North Pole and the Canadian Basin. GEM and Hg(II) species in air was measured using a Tekran 2537B instrument coupled to an 1130/35 mercury speciation system and the average GEM concentration during the campaign was 1.4 ± 0.2 ng m-3. The average concentrations of Hg(II) and particulate Hg(II) in air were found to be 1.6 ± 2.4 and 2.4 ± 2.0 pg m-3, respectively.

DGM was measured using an automated method and the seawater was sampled from the bow water system of the ship having a water intake at an approximate depth of 8 m. The extracted equilibrium concentration of DGM in the outgoing air was measured using a Tekran 2537A instrument. The average DGM concentration was 40 ± 19 pg L-1 with higher concentrations found when passing through sea ice (48 ± 15 pg L-1) than in open water (19 ± 4 pg L-1). The higher surface DGM concentrations found under sea ice was due to a capsuling effect.

The surface of the Arctic Ocean was found to be supersaturated (438 ± 196 %) and an average air-sea flux rate of 1.52 ± 2.27 ng m-2 h-1 was calculated, indicating a net evasion of Hg(0) from open sea surfaces in the Arctic Ocean.

RO-015

CYCLING OF METHYLATED MERCURY SPECIES IN THE CENTRAL ARCTIC OCEAN

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Extreme warming events are currently being observed in the Arctic with November air temperature being 20°C higher than historic normal and the sea ice coverage in the early winter month being at record lows. As the sea ice extent decreases, new areas, including the central Arctic Ocean, are made more accessible and will become attractive for the commercial fishing industry. Concerns are now being raised for a future "gold-rush" as international regulations are inadequate to protect the ecosystem and human health. One major concern is methylmercury (MMeHg). Human health concerns related to the pollution of the pristine environment of the Arctic by Mercury (Hg) and MMeHg may be triggered by climate change. However, fundamental understanding of the cycling of methylated mercury species in these environments, including the central Arctic Ocean, is lacking and more study warranted. The central Arctic Ocean covers around 40% of the Arctic Ocean area but remains largely unexplored when it comes to the occurrence and cycling of methylated mercury species. In this presentation, we will present data on mono- and dimethylmercury (MMeHg and DMeHg, respectively) in ice, brine, meltwater and sea water collected in 2016 during the SWEDARCTIC 2016 expedition, and for comparison, total methylmercury (MeHgT; i.e. MMeHg + DMeHg) collected in 2007 during the LOMROG expedition. Both expeditions were performed onboard the Swedish IB Oden and coordinated by the Swedish Polar Research Secretariat (SPRS). Our studies cover the central Arctic Ocean from the Canada Basin to the Nansen Basin. The concentrations of DMeHg in the polar mixed layer were unexpectedly low and calculated fluxes of DMeHg from and to the polar mixed layer suggest it to be a sink for DMeHg. We further suggest the degradation of DMeHg to be a major source of MMeHg in the surface waters. The concentrations of MeHgT in seawater in 2007 and 2016 were similar to concentrations previously reported from the central basin but lower than the concentrations typically reported from the Canadian Arctic Archipelago. One contributing factors to the lower MMeHg concentration in the central basin could be an overall lower primary production and thus lower re-mineralization and in situ formation of MMeHg in the deeper waters of this region.

RO-016

MERCURY IN THE NORTH ATLANTIC AND ARCTIC OCEANS - RESULTS OF THE 2014 GEOTRACES GEOVIDE, 2015 GEOTRACES TRANSARC II & 2016 GEOTRACES GRIFF CRUISES

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We will present the combined results of the 2014 French GEOTRACES GA01 GEOVIDE cruise (North Atlantic), the 2015 German GEOTRACES GN04 TransArc II cruise (Central Arctic Ocean) and the 2016 German GEOTRACES GN05 GRIFF (Fram Strait) cruises. Full water column profiles were sampled using ultra-trace clean rosettes and total mercury (Hg) was determined directly on board. We find consistent surface depleted profiles in the North Atlantic Ocean, averaging overall 0.57 ± 0.2 pM (n = 527), while we observe surface enrichments in the Arctic Ocean (1.01 ± 0.48 pM, n = 54, 0 – 20 m) and Fram Strait (1.44 ± 0.39, n = 30, 0 – 20 m). Fram Strait is the only deep connection between the North Atlantic and the Arctic Ocean, were warm saline Atlantic waters transit into the Arctic as the West Spitzbergen Current. At the same time, a great part of the immense Arctic fresh water excess is exiting as the East Greenland Current and sea ice. We find that Hg concentrations (0.65 ± 0.19 pM, n = 280) of the Atlantic-sourced water mass present in the Arctic Ocean below the halocline (>200 m) matches well the North Atlantic average. The East Greenland Current transports the Hg enriched surface waters southwards, out of the Arctic Ocean. Hg inputs to the Arctic Ocean were until now based on measurements from the North Atlantic and modeled seawater flows. Our refined measurements will assist in narrowing down the relative contributions of Hg fluxes to and from the Arctic Ocean.

We will make use of the combined data sets of all three cruises to refine the previously published Arctic Ocean Hg budgets using numerical model evaluations based on a coupled 3-D atmosphere-ocean simulation (GEOS-Chem coupled to the MITgcm).

2d-1: Mercury fate in aquatic and terrestrial food webs

RO-017

MECHANISTIC INFORMATION ON HG UPTAKE BY FRESHWATER BIOFILMS UNDER CONTROLLED CONDITIONS

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Freshwater biofilms are natural assemblage of microorganisms, such as microalgae, bacteria and fungi, which live together in symbiosis in an exopolymeric substances matrix. Besides their implication in the ecology and biochemistry of aquatic systems, biofilms are defined to be one of the entrance of mercury (Hg) along the trophic chain. The objective of the present study was to investigate the kinetics of Hg accumulation (total and non-extractable) in biofilms of different compositions under controlled conditions during 24 hours. To that end, biofilms were grown on microscopy glass slides for 85 and 127 days in microcosms supplied with Geneva lake water and exposed for 24 hours to about 150 pM Hg concentrations (precisely measured). Both biofilms were examined for their Hg content as a function of the exposure time (10 min, 30 min, 1 h, 4 h, 6 h, 8 h and 24 h). In addition, biomass, chlorophyll content and the abundance of specific genes (16S. merA and HgcA) were also analyzed in both biofilms. Physico-chemical parameters of the exposure water were characterized such as temperature, pH, anion/cation, dissolved organic matter, dissolved Hg concentrations. For both biofilms, Hg accumulation was rapid (<10min) and total Hg concentrations in biofilms were comparable in the first hours of exposure. However, after 24 h exposure, these concentrations were 886 ± 179 pmol gdw-1 and 1528 ± 73 pmol gdw-1 for the young and old biofilm, respectively. For both biofilms, non-extractable Hg content was modelled using a non linear pseudo first order one-compartment model. The uptake rate constant of the young biofilm was 10 times higher than for the old biofilm. Furthermore, Hg accumulation in the young biofilm reached a plateau, allowing the calculation of a clearance rate constant, whereas Hg content in the old biofilm remained linear. These results might be explained by a larger thickness of the EPS matrix in the old biofilm, which was assessed with the lower biomass but similar surface coverage area in the young biofilm than in the old biofilm, indicating that the old biofilm grown in the third dimension. The thicker matrix of the old biofilm might thus limit the diffusional flux of Hg from water to the microorganisms, decreasing the constant Hg uptake rate. The 24h-Hg exposure was additionally found to induce a decrease of chlorophyll content in both biofilms, suggesting a high impact of microalgae. The present study demonstrates that biofilm composition influence Hg accumulation.

RO-018

TROPHIC FATE OF INORGANIC AND METHYL-MERCURY IN A MACROPHYTE-MACROINVERTEBRATE FOOD CHAIN

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Dietary transfer of mercury (Hg) is considered as having the highest importance for its effects on higher trophic animals, but few studies have addressed the precise factors controlling this transfer as well as its mechanisms and characteristics. Recently we observed that Hg found in cell walls of macrophytes were a significant source of Hg to gammarids. Because cell wall constituents are recalcitrant by nature and are expected to remain for a long period in sediments after plant decay, we made the hypothesis that benthic organisms might as well be exposed to Hg found in tissues of macrophyte. Here, we assess how the Hg accumulated in a representative macrophyte, Elodea nuttallii was transferrable to Chironomus riparius, chosen as surrogate species for benthic organisms. Three different concentrations, comparable to those found in macrophytes from unpolluted and contaminated sites, of inorganic Hg (IHg) and methyl-Hg (MMHg), and 2 compartments (cell wall, intracellular) were used as unique food source for C. riparius. Toxicity, bioaccumulation and subcellular toxicokinetics were measured.

We observed an effect of plant intracellular Hg on chironomid growth, caused by both IHg and MMHg at the higher concentrations (11.69 ± 4.91 mg·kg-1). Bioaccumulation measured in C. riparius revealed that MMHg was more transferable than IHg in our conditions. Data also support that Hg in cell walls was more transferable than intracellular Hg, when chironomids survived the treatment. Besides, after 10-d-long exposure, MMHg was predominantly found in MMHg form in the cytosolic fraction (S), considered as the metal-sensitive fraction, while IHg showed similar concentrations in S and insoluble debris (P) fractions. After 2-day-long depuration, only MMHg showed a BAF > 1 both in S and P fractions in C. riparius. Our data support that both intracellular and cell wall accumulated Hg are dietary transferable from macrophytes to macroinvertebrates. Besides, both IHg and MMHg are dietary transferable from macrophytes to macroinvertebrates, but MMHg is more transferable to sensitive subcellular targets in chironomids than IHg, in line with field studies showing a 2- to 4-fold higher transfer of MMHg than IHg in food webs. Our data hence point out the macrophytes as a new important source of Hg transfer to benthic consumers in local food webs to be considered for enhancing aquatic environment protection.

RO-019

BIOACCUMULATION OF MERCURY IN INVERTEBRATES IN CONTAMINATED AND NON-CONTAMINATED RICE-PADDY ECOSYSTEMS OF CHINA: A PULSE OF METHYLMERCURY TOWARDS THE END OF THE RICE GROWING SEASON

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Mercury (Hg) is a toxin shown to have serious health effects for humans and animals. While Hg is a global problem due to the world-wide distribution of anthropogenic Hg emissions, and local pollution from industrial processes, Asia represents the majority of current and future emissions and hence requires particular attention in Hg research. In this study in China, we concentrated on spiders, can play an important role in the bioaccumulation of Hg in the food web, as they themselves are carnivorous and then are consumed by birds, in rice paddies ecosystems, known to be vulnerable ecosystems for Hg bioaccumulation. In 2014 we sampled soil and invertebrates over a gradient of distances from the abandoned mines and at a control site also in Guizhou Province, but without a history of mercury mining, at the end of the rice harvest. In addition, to test the hypothesis that Hg accumulation in the ecosystem is seasonal, we collected separate samples at different seasons in 2015. We measured THg and MeHg levels in range of invertebrates. In the 2014 data, we uncovered a pattern of THg and MeHg concentrations in spiders and grasshoppers that decreased with increasing distance from the abandoned mines. For all species, the distance to the mines significantly influenced THg. Patterns in the percentage of THg that was MeHg were complicated. The spider species varied in their THg and MeHg levels, with orb weavers generally have higher concentrations, and this pattern was correlated to their trophic levels, as measured by C and N stable isotopes. In the 2015 data, THg concentrations in soil were stable during two seasons, but soil MeHg concentrations were significantly higher when rice was nearly mature. For all invertebrate species, and all sites, there was a strong seasonal increase in MeHg. While there was also an increase in THg concentrations, that increase was less than the increase in MeHg (MeHg was on average 2.15 times higher at harvest, compared to THg, that was on average 1.52 times higher). These results indicate that there is a pulse of MeHg in the ecosystem towards the end of the rice growing season, which through spiders may flow into the vertebrate component of the food web. We argue that multinational studies need to be conducted in rice-based ecosystems throughout Asia to further investigate whether there may be an undocumented loss of biodiversity related to Hg local pollution and deposition in Asia.

RO-020

THE SUITABILITY OF TOTAL MERCURY AS A SURROGATE FOR METHYLMERCURY IN AQUATIC MACROINVERTEBRATES DEPENDS UPON THE FEEDING GROUP OF INTEREST

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Methylmercury (MeHg) is the toxic and bioavailable mercury species of greatest interest to monitor in aquatic biota, but laboratory analysis of MeHg in biological tissue is much more expensive than is analysis for total Hg (THg). However, when the percentage of MeHg relative to THg (hereafter MeHg%) is high and well-established, as in fish tissue (generally > 90%), THg analysis results can adequately represent MeHg concentrations. Aquatic macroinvertebrates have great potential as MeHg sentinels in monitoring programs. They are important in MeHg trophic transfer to fish, and are often abundant and relatively easy to collect. However, macroinvertebrates are not widely used in MeHg monitoring because the suitability of THg as a MeHg surrogate in macroinvertebrate tissues has not been empirically established. The U.S. Geological Survey (USGS), with support from the New York State Energy Research and Development Authority, conducted a study to evaluate the suitability of THg as a MeHg surrogate for macroinvertebrates from streams in undeveloped settings by documenting taxonomic, spatial, and temporal variation in MeHg%. MeHg and THg concentration data from more than 300 samples were compiled from published USGS studies conducted in the Adirondack Mountain region of New York (nine streams) and, for geographic comparison, from Coastal Plain streams in South Carolina (four streams). The macroinvertebrate taxa from these samples were categorized by scraper, shredder, collector-gatherer, filterer, omnivore, and predator functional feeding groups (FFGs). Median MeHg% in Adirondack samples ranged from 35% in scrapers to 92% in predators, and varied significantly among feeding groups (Kruskall-Wallis test, F=103, $p<0.0001$). MeHg% in predators, mainly dragonflies (Odonata: Aeshnidae and Libellulidae) from Adirondack and Coastal Plain streams was typically high (>90%) and exhibited minimal taxonomic, spatial

and temporal variation. In contrast, MeHg% within most of the lower FFGs considered was highly variable. Median MeHg% in the northern case-maker caddisfly (Trichoptera: Limnephillidae), a shredder, collected from six Adirondack sites ranged from 18% to 72%, and differences were highly significant (F=18.0, $p<0.0001$). Median MeHg% in the flat-head mayfly (Ephemeroptera: Heptageniidae), a scraper, collected from five Adirondack sites ranged from 28% to 55%, and was significantly higher in summer than in spring from the same site (Wilcoxon rank-sum test, $p<0.005$). These results indicate that THg has good potential to function as a surrogate for MeHg in dragonflies and other predatory aquatic macroinvertebrates in streams of largely undeveloped watersheds, but MeHg analyses are warranted for taxa that feed at lower trophic levels.

RO-021

THE DRAGONFLY MERCURY PROJECT: A NATIONAL SCALE EVALUATION OF VARIATION IN BIOSENTINEL MERCURY CONCENTRATIONS AND LANDSCAPE DRIVERS ACROSS US NATIONAL PARKS

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The Dragonfly Mercury Project spans more than 200 unique locations across over 60 national parks throughout the US. Since 2014, parks have sampled dragonfly larvae for total mercury (THg) and methylmercury (MeHg) as well as surface-water (filtered THg and MeHg, DOC, sulfate, SUVA, and pH), and sediment (THg and MeHg) to determine: (1) baseline Hg concentrations in national parks prior to implementation of national and international mercury use and emission controls; and, (2) which habitats and catchment characteristics influence vulnerability to Hg accumulation in foodwebs. Dragonfly larvae are useful bio-sentinels for Hg spatial patterns because they are widespread in freshwaters, exhibit high site fidelity, and as predators, contain almost all of their Hg as MeHg (83% in this research). In an initial subset of the data including 127 freshwater lakes, ponds, wetlands, streams, and river sites in 34 national parks, THg in dragonfly larvae was 141.1±2.5 (mean±SE) ppb, dry weight (dw). We observed 76-fold variation between the sites with the greatest (>1000 ppb, dw) and least (~20 ppb, dw) mean dragonfly larval THg concentration across parks, and up to 44-fold variation among sites within a single park, highlighting the importance of spatial variability at the scale of individual water bodies. Preliminary analyses in Olympic and Acadia National Parks, where >10 water bodies of varying size, type, and hydroperiod were sampled, indicated that stream sites had the greatest dragonfly THg concentrations as compared to wetlands, ponds, and lakes. We observed taxonomic variation in dragonfly MeHg:THg only for one of the six families present in these parks. Larvae of the family Aeshnidae, which tend to be aggressive predators that can consume larval frogs and small fish, generally had greater MeHg:THg than larvae of other families. Linking water chemistry parameters with dragonfly and sediment THg allows for comparison of modeled vulnerability to methylation with actual geographic patterns that include these point-specific, layered MeHg production drivers. Although use of dragonfly larvae as bio-sentinels for Hg continues to be a promising approach and allows for Hg assessment at sites that are fishless, it is important to statistically account for habitat, taxonomic, and ontogenetic differences in interpreting and comparing data among sites.

RO-022

PATTERNS OF MERCURY BIOACCUMULATION IN INVASIVE LIONFISH (PTEROIS VOLITANS/MILES) FROM CURACAO

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Since the 1980s, predatory Indo-Pacific lionfish (Pterois volitans/miles) have successfully invaded and rapidly spread throughout the western Atlantic Ocean and Caribbean Sea. Invasive lionfish can be detrimental to coral reefs and fisheries, and efforts to control lionfish population size include targeted removals and spearfishing derbies. Spearfishing and consumption of lionfish are increasingly popular and effective tools for maintaining lionfish populations at reduced levels. However, few studies have examined whether consumption of lionfish poses any danger to human health through exposure to contaminants, such as mercury. Here, we analyzed lionfish collected along the southern coast of Curacao, relative to the island's oil refinery (Isla Refinery), for total mercury (THg), stable isotopes of nitrogen ($d^{15}N$) and carbon ($d^{13}C$), and stomach contents. Fish ranged in size from 86 and 331 mm standard length and total mercury concentrations ranged from 0.008 to 0.106 ppm. THg significantly increased with fish length and fish body condition, suggesting bioaccumulation of mercury as lionfish age. THg also increased linearly with $d^{15}N$, but not $d^{13}C$, suggesting lionfish feeding on higher trophic level prey resulted in greater mercury bioaccumulation, but different carbon sources did not differ in mercury concentration. Stomach content analyses complement these findings, as larger lionfish with higher THg consumed more vertebrate prey items than smaller, younger lionfish. THg did not significantly differ across sampling sites, indicating that Isla Refinery has no direct impact on lionfish mercury levels in Curacao. However, sampling site was related to $d^{15}N$; specifically, Punda, a sampling site located directly off the coast from Isla Refinery, had significantly higher $d^{15}N$ than all other sampling sites. $d^{13}C$ was significantly different across sampling depths and, in particular, was enriched in lionfish captured at the shallowest (5-15m) depth range, depths approximately shallower than Curacao's fringing reef. Overall, these results indicate that lionfish around the island of Curacao contain low concentrations of total mercury, even in the presence of a local oil refinery.

RO-023

CONTAMINANTS AND NATIVE FISH CONSERVATION IN THE UPPER COLORADO BASIN: THE FORGOTTEN STRESSORS, MERCURY AND SELENIUM

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Native fish populations, including four federally endangered fish species (Colorado Pikeminnow, Bonytail, Humpback chub, Razorback sucker), in the Upper Colorado River Basin (UCRB), have endured many threats, including altered natural flow and thermal regimes, fragmentation of habitat by dams, invasions by nonnative species, and climate change. Exposure to contaminants has been understudied in the UCRB, largely because of its remoteness and high proportion of federally managed lands. However, global transport of mercury (Hg) and deposition within the basin has become a concern. In addition, the UCRB has naturally high background concentrations of selenium (Se) in the surrounding soils and bedrock. Within the basin, mining and combustion of coal may be a local source of Hg while an expansive conversion of arid land to irrigated land has exacerbated transport of Se to the riverscape. Both Hg and Se can be toxic to wildlife, but in combination Se may abate Hg toxicity. In response to these concerns, the U.S. Geological Survey has compiled and analyzed a historical database of fish tissue Hg and Se concentrations for the UCRB. Over 2000 fish tissue samples have been collected basin-wide since 1962; however, 73% of these samples were collected in only 8 of the last 26 years, and only 12% were from federally-endangered fishes. Historically, average basin-wide Hg concentrations in two fishes of conservation concern (i.e., Roundtail Chub and Colorado Pikeminnow) were >2.4X the US EPA human health standard of 0.3 ppm; whereas only 1 native fish species, speckled dace, averaged above the 2016 US EPA tissue standards for Se. Considerable geographic variability in Hg and Se concentrations in fish was observed among the eight UCRB subbasins. The White-Yampa River and the Lower Gunnison River basins had the highest average (pooling across species) Hg and Se concentrations (respectively). There was also considerable variability in Se:Hg ratios among subbasins, however typically ratios exceeded 5. These relatively high Se:Hg ratios suggest that Hg toxicity is abated by Se, however, locally high Se concentration may pose risks to native fish. Preliminary findings suggest that some imperiled fishes of the UCRB face potential risks associated with high Hg and Se exposures. In 2016, we augmented the historical Hg and Se data by collecting more than 1000 samples, including >300 from native endangered species. These samples and those collected in the coming years will help identify if Hg and Se exposures pose risks to native fishes of the UCRB.

RO-024

IMPACTS OF CLIMATE AND LAKE BROWNING ON MERCURY CONCENTRATIONS IN FISH – AN ANALYSIS OF RESAMPLED PERCH POPULATIONS IN SCANDINAVIA

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Mercury (Hg) contamination in freshwater fish is a severe environmental problem throughout the world, including the Scandinavian region. Health advisory limits are often exceeded in perch (Perca fluviatilis) in Sweden and Norway, even in remote boreal lakes. Historically deposited and catchment stored long-range transported atmospheric Hg is the main pollution source to the lakes. The last 20-30 years, fish Hg concentrations show patterns – including long-term increases – that currently lack an explanation. Generally, absence of data from the same lakes over time leads to confusing temporal patterns drawn from spatial variation.

We designed a sampling campaign to revisit lakes with historical data on Hg in fish along a north-south gradient in Norway and Sweden. The lakes have been subject to varying degree of browning and climate warming, enabling us to test hypotheses on factors driving Hg levels in fish. In freshwaters, elevated concentrations of Hg appear to be connected to humus-rich waters, which makes a connection between the recent rise in surface water colour and increased Hg in fish plausible. Similarly, a warmer climate may potentially affect Hg concentrations in top predators through a range of direct and indirect processes.

We selected 27 lakes that 1) had Hg in fish data available from the 1990s; 2) were located in three different climatic regions, i.e. South-boreal, Mid-boreal and Subarctic (from 59.0° N to 69.5° N); 3) had gradients in dissolved organic carbon (DOC) concentrations, pH and productivity within each region. Sampling was conducted during the autumn of 2016. We tested hypotheses on the main drivers of temporal trends of Hg in fish in Sweden and Norway by collecting data on catchment characteristics, water chemistry, fish, gridded downscaled weather data, and reconstructed DOC trends based on monitoring data and process-understanding of DOC drivers.

All lakes were sampled in the early 1990s, the 2000s and 2016. Temporal trends were identified using a covariance analysis, creating general linear models. Explanatory variables included season, year, fish morphology and stable isotopes (δ15N and δ13C), in addition to fatty acids where available, to test for dietary preferences. We will show robust tests of hypotheses on effects of climate and browning on Hg in fish based on these datasets. In addition, we will be able to test effects of short-term climatic variation on annual and seasonal variation in Hg in fish from a sub-set of lakes, using growth and trophic status as additional variables.

2e: Artisanal Small-scale Gold Mining (ASGM): Current and historical emissions, current practices and future projections

RO-025

ASSESSMENT OF MERCURY LOSSES DURING THE THERMAL DECOMPOSITION OF SILVER AMALGAM USING RETORTS

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The misuse of mercury in artisanal small-scale gold mining gained notoriety with the consolidation of the Minamata Convention (2013). There is a worldwide concern for improvements in the processes used for extracting gold in such places. One of the proposals is the use of retorts during the thermal decomposition of gold amalgam. Therefore, this study aimed at developing an occupational exposure assessment methodology for those operators before such equipment, and, at the same time, to evaluate the possibility of dragging precious metals during the pyrolysis process. According to preliminary results, the retort tested showed significant emissions of mercury to the atmosphere and so did precious metal. However, new trial tests shall be accomplished for validating those previously obtained results, taking into account, in these additional tests, the performance evaluation of different retort designs. Finally, as an attempt to validate the proper retorting temperature range for better decomposing the aforementioned amalgam a thermo-gravimetric analysis were run, which generated the right figures to use the proper thermo-decomposing temperature so as to avoid losing precious metals with the mercury vapor.

RO-026

NANOGOLD ON POROUS GLASS AS A PASSIVE SAMPLER FOR MONITORING OF GASEOUS ELEMENTAL MERCURY IN ARTISANAL GOLD MINING

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Mercury contamination is a major working hazardous in artisanal gold mines in developing Countries, particularly in Africa, Asia and South America. There are no portable and cheap methods able to alert workers of mercury exposure on site in remote locations.

In this work, a miniaturized mercury sampler prepared by the direct reduction of gold into the porous nanostructures of Vycor® glass (PVG) is introduced. Mercury retention on the PVG/Au sampler induces significant color changes, due to the formation of Au-Hg amalgam that affects the surface plasmon resonance characteristics of the material. The color change can be easily verified by eye and quantified based on the analysis of the RGB channels obtained from pictures of the sampler. Therefore, the sampler can be easily deployed in remote areas and the gold exposure can be evaluated using a somethings as simple as a cell phone camera.

The PVG/Au sampler was prepared in two steps: impregnation of PVG discs (0.6 cm Ø) with HAuCl solution, followed by the direct reduction in situ of AuCl4- to Au0. The presence of nanogold was readily detected by the red color of the PVG/Au disc. The PVG/Au was analyzed by high-resolution transmission electron microscopy (HRTEM). The amount of gold deposited in the PVG/Au discs was determined by ICP-MS. Mercury retained on the samplers, before and after exposure, was quantified by Direct Mercury Analyzer®.

The samplers were first exposed to Hg vapor (~2 ppmv) for different times (8 to 48 h) and these laboratory experiments showed the viability of using PVG/Au as passive sampler for monitoring of Hg0. The retention of mercury by PVG/Au samplers was monitored by Red-Blue-Green analysis of images of the samplers and by using ultraviolet-visible spectroscopy. PVG/Au samplers were also deployed in an Artisanal and Small Scale Gold Mining (ASGM) area in Burkina Faso and it was able to indicate mercury exposure. The amount of mercury quantified in the samplers for all miners was higher than the current personal exposure limit for Hg0 set by the US Occupational Safety & Health Administration (OSHA), which is 0.1 mg m-3 (~12 ppbv in air), indicating an unhealthy work environment. The nanogold sampler described here is therefore a potential tool to that can quickly and cheaply evaluate mercury exposure in work conditions of ASGM sites and other settings.

RO-027

ASSESSING THE STATUS AND PERFORMANCE OF MERCURY CAPTURE DEVICES TO REDUCE GOLD SHOP EMISSIONS, RELEASES, AND ASSOCIATED EXPOSURES

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Artisanal and small-scale gold mining (ASGM) is a major source of global mercury pollution. Miners often add mercury to ore to separate the gold, and then take this amalgam to a gold shop where the mercury is driven off at high temperatures. An estimated 50,000gold shops serve the ASGM community as a key step in the gold supply chain. In some cases, simple devices such as water-based box condensers and pipe

retorts are used to capture the mercury during amalgam burns. If not captured, mercury can exceed 1,000mg/m3 inside gold shops, which is then released to ambient air. Chronic human exposures to mercury can harm the central and peripheral nervous systems and other organs and systems.

To help address this issue, the U.S.Environmental Protection Agency (EPA) has led efforts to develop and implement a mercury capture technology to reduce emissions in gold shops. In collaboration with Argonne National Laboratory, a simple mercury capture system (MCS) was designed that would be easy to make using local materials and capabilities. The MCS consists of a steel drum that houses a fan, which draws air from above the amalgam burn through slotted baffle plates on which the mercury condenses and then collects at the bottom of the drum for removal. The system was deployed in more than thirty gold shops across Peru and Brazil from 2005-2010. Indoor test results indicated the MCS achieved mercury removal efficiencies of 80% and higher.

EPA, Argonne, and Mercer University are collaborating to assess the status of MCSs and other mercury capture devices in gold shops. The goal is to increase understanding and awareness of such devices as a measure that could substantially reduce emissions and releases from gold shops, thus reducing worker exposures and exposures of people in communities nearby. The collaboration will explore a number of factors around the presence and management of mercury capture devices in gold shops, including:

- Insights into uptake and operational factors;
- Design, fabrication, installation, and operation of such devices;
- Collection and disposition of the captured mercury;
- Costs, benefits, and incentives; and
- Supplemental information, such as additional design details and mercury measurements.

Possible future activities include exploring the potential role of citizen science, and of mercury capture technology as a strategy option for reducing mercury emissions as part of larger national efforts, with consideration as a technological strategy for addressing targets identified in National Action Plans for ASGM activities.

RO-028

DEFORESTATION DURING ARTISANAL AND SMALL-SCALE GOLD MINING EXACERBATES MERCURY MOBILIZATION IN MADRE DE DIOS, PERU

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Artisanal and small-scale gold mining (ASGM) is a significant contributor to mercury (Hg) contamination and deforestation, particularly in the Colorado River watershed in Madre de Dios, Peru. Within the Colorado River watershed, mining and deforestation have increased dramatically since the 1980s and have been largely concentrated in the Puquiri River, a tributary of the Colorado River. Field sampling in Feb 2015, Apr 2016, and Jun 2016 identified a strong correlation between Hg and suspended solids concentrations, with especially high suspended solids concentrations downstream of ASGM activity. This result suggests that Hg transport in this region was facilitated by soil mobilization and runoff. In order to understand how ASGM activity in the Puquiri affects sediment and Hg mobilization from the watershed over time, we employed a watershed-scale soil mobilization model using satellite imagery from 1986 to 2014. The model estimated that soil mobilization in the Colorado River watershed increased by 2.5 times during the time period, and increased by six times in the Puquiri subwatershed, leading to between 10 and 60 kg of Hg mobilized in 2014. If deforestation continues at its current exponential rate through 2030, soil and heavy metal mobilization may increase by five times. This research shows that deforestation associated with ASGM can exacerbate soil mobilization and Hg contamination.

RO-029

FLUVIAL MOBILITY OF MERCURY, CYANIDE AND OTHER HEAVY METALS IN THE PUYANGO-TUMBES RIVER BASIN, ECUADOR-PERU

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In Portovelo-Zaruma in southern Ecuador, 87 gold processing centers line the banks of the Puyango-Tumbes River, producing an estimated 6 tonnes of gold/a. Each of the plants processes gold using a combination of mercury amalgamation and/or cyanidation, resulting in an estimated 1.6 million tonnes/a of tailings enriched with 2040 tonnes/a of cyanide, 0.243 tonnes/a of mercury and other heavy metals being discharged into the Puyango-Tumbes River, that crosses from Ecuador to Peru and ends up in the Pacific Ocean. The results showed that the majority of the water and sediment samples collected from the Puyango-Tumbes River had elevated concentrations of total arsenic, cadmium, copper, lead and zinc, exceeding the CCME (Canadian Council of Ministers of the Environment) Long Term Effect thresholds for the Protection of Aquatic Life. At monitoring points immediately below the processing plants, total arsenic concentrations exceeded the threshold by 3000 times in solution in surface waters and 740 times in sediment. Even over 140 km downstream, arsenic concentrations in water and sediment were still well above the permissible limits, especially in the sediments. The highest total cadmium concentrations were 555 times over the guideline in surface waters and 120 times over the CCME standard in sediments, which raises concern about contamination of aquatic organisms. The highest copper concentrations in surface waters exceeded the threshold by 3567 times and in sediment by 85 times. The highest lead concentrations were 840 times over the guideline in surface waters and 27 times in sediment. Steps should be taken to reduce lead exposure, especially in regards to potential bioaccumulation in aquatic biota. Free cyanide concentrations were high in surface waters of the river for 50 km below the processing plants, with the highest concentration 13,560 times above the CCME standard of 5 µg/L and 1695 times above the 24-hour LC50 concentration (50 percent fatality) of 40 µg/L free cyanide for some fish species. The highest total mercury (THg) concentrations in sediments were found within a 40-km stretch downriver from the processing plants, with levels varying between <0.03-30.8 mg/kg during the dry season and 1.8-45.1 mg/kg during the wet season, with most concentrations above the CCME Probable Effect Level of 0.5 mg/kg. Data from mercury isotopic analyses support the conclusion that mercury use during gold processing in Portovelo-Zaruma is the source of Hg pollution found far downstream in the Tumbes Delta in Peru, 160 km away.

RO-030

CO-EXISTENCE OF ARTISANAL AND CONVENTIONAL MINERS: A GOOD SOLUTION FOR FORMALIZATION

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The formalization of artisanal gold miners in developing countries has been seen by governments and international agencies as the main way to eliminate bad practices, including mercury pollution that has reached 1600 tonnes/a. It is clear that formalization generates more control and tax revenue for the governments, while providing miners with a legal mining title and access to credit. However, in reality, these benefits are often not favorably viewed by the miners, as the complicated bureaucracy of banks and governments does not make it easy to access credit. In addition, it is observed in many countries that the main mercury polluters are the processing centers, which normally are allowed to operate freely. Without enforcement of legal and environmental regulations, formalization does not provide any solution. This study shows how the UBC Mining Engineering Department is currently working in Colombia with 3 conventional large-scale gold mining companies that have artisanal miners in their concessions, in order to establish initiatives for the implementation of a small mine and plant. This type of co-existence and joint venture between conventional mining companies and artisanal miners allows for the transformation from widespread atmospheric and fluvial contamination with mercury and cyanide to the adoption of Hg-free technologies. The co-existence model has a strong bottom-up component, where it is crucial to assess the needs of the miners, their motivations to change their rudimentary practices and their ability to understand and implement cleaner procedures. Once these factors are adequately assessed, a strong organizational and educational program is conducted with pre-selected leaders. In parallel, a small area of the companys gold deposit is decided upon for the artisanal miners to work using clean and safe practices, as well as analysis of an appropriate area for construction of a small plant (100-200 tonnes of ore/day). Concurrently, metallurgical testing is conducted in the lab to establish the processing parameters of the plant. A pre-feasibility study is then initiated to determine the economic viability of implementing the mine and plant using gravity and flotation systems, followed by intensive cyanidation or sale of concentrates to a third party. The various business models of operation of this new enterprise is discussed with the miners. In doing so, uneducated, subsistence miners living under the poverty line can improve their standard of living, reduce health impacts and contribute to more responsible environmental stewardship.

RO-031

THE MINAMATA CONVENTION AND GOVERNING MERCURY USE IN ARTISANAL AND SMALL-SCALE MINING IN GHANA

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This paper examines the impact of the Minamata Convention's legality, issue focus, and linkages on activities of transnational networks and intergovernmental bodies in the governance of mercury use in artisanal and small-scale mining (ASM). Earlier voluntary regional efforts and national policies have been unsuccessful at curbing the production, supply, and use of the chemical in industrial processes, including ASM. The release of mercury and its compounds into the environment through human activity has far-reaching health implications, and ASM is now the highest source of anthropogenic release of mercury into the environment. As a widespread economic activity globally, mercury-using ASM poses a major threat to human security. Concerned, crafters of the legally-binding global convention on mercury dedicated a whole article (Article 7) to mercury use in ASM. The governance of mercury use under this convention is novel and different from earlier efforts in three main respects: 1) its global legality; 2) its emphasis on human security concerns; and 3) the linkages it generates across scales and two governance regimes. I describe this as the legality-issue-linkages (LIL) framework. Using qualitative and quantitative data gathered from intergovernmental bodies and transnational networks, and focusing on Ghana, the paper presents results from field research examining the impact of the LIL framework on national and local governance of the use of mercury in ASM.

RO-032

ARTISANAL AND SMALL-SCALE GOLD MINING IN CÔTE D'IVOIRE: MERCURY ESTIMATES AND CONTRAST WITH LOCAL REGULATIONS

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The artisanal and small-scale gold mining (ASGM) sector is the largest anthropogenic source of mercury to the environment with around 1,400 tons of mercury released annually. The Minamata Convention on Mercury, which opened for signature in 2013, contains an entire article dedicated to ASGM. This article requires ASGM countries to create National Action Plans to reduce, and where feasible, eliminate mercury use in ASGM. Under these National Action Plans, countries will be required to take technical measures to reduce or eliminate mercury use, and to create policy frameworks on formalization, trade, public health, multi-stakeholder engagement and education, to support the transition of ASGM to a mercury-free and more economically productive sector. Côte d'Ivoire, a West Africa country with 40% of the Economic Community of West Africa States' (ECOWAS) economy, has signed the Minamata Convention on Mercury on October 11, 2013. In preparation of the ratification, enabling activities have been performed to assist the government in the process and have an early implementation. As part of that process, a national mercury inventory in ASGM was conducted based on field studies and research that includes socio-economic data, direct mercury use measurements, semi-structured interviews, household survey data, and the size of the secondary economy of involved communities. This research found that 11,275 of artisanal miners, coming mainly from all ECOWAS countries, are using 2.3 tons Hg/year and this mercury is being entirely released in the environment via open burning of the amalgamated concentrate gold ore. In many ECOWAS states, the national regulation and many sub-regional regulations prohibit mercury use in ASGM. Thus, it appears that the implementation of Minamata Convention in all ASGM - ECOWAS countries will be a challenging process that will require a deep reform of ASGM sector to comply with the Convention provisions.

2j: Mitigating Mercury Bioaccumulation in Contaminated Aquatic Ecosystems

RO-033

ECO-REMEDIATION STRATEGY FOR SOILS HIGHLY CONTAMINATED WITH MERCURY – FIELD STUDIES INSIDE CHLOR- ALKALI PLANT

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The main Polish sources of mercury atmospheric emissions are combustion of fossil fuels, mainly coal, cement production and industrial production processes, in particular the mercury cell chlor-alkali processes for production of chlorine and caustic soda, smelting of ferrous and non-ferrous metals, especially zinc and copper as well as consumption-related discharges. When the critical limit for Hg in case of Hg contaminated soils is taken into consideration (30 ppm), the areas inside the chlor-alkali plants (CAP) are characterized by Hg concentration range with the median value from 40 ppm up to 557 ppm. Gaseous emission of Hg from CAPs was considered to be one of the most important point sources of anthropogenic mercury in Poland.

Not only Europe needs safe and cost-effective solutions for the permanent storage of elemental mercury inside chlor-alkali plants. The solution is expected to be environmentally sound and economically viable. Phytoremediation, an approach that is possible to use plants physiological properties for soil pollutant degradation, stabilization or extraction is taken into consideration also in relation to mercury problem.

Presented investigations are related to the changes in mercury cycling after soil amendment application. We hypothesized, that soil appropriate additives have positive impact on concentrations of bioavailable mercury in soil solutions, bioaccumulation and volatilization. Biogeochemical processes were analyses based on lab scale treatability study (lysimeter experiment) and plot scale experiment located in natural conditions on the selected area inside one of the CAP. Experiments were planned to test phytostabilization and aided phytostabilization of mercury contaminated soil.

Soil and soil solution samples were analyzed for their pH, EC, content of bioavailable fractions (soil water-soluble and exchangeable mercury fractions). Selected plant species (dicots and monocots) and soil additives (sulphur, zeolites) were tested for their phytostabilization effectiveness.

Additives were also analyzed as the potential soil factors stimulating local biodiversity and natural succession from outskirts modulate dominant plant species, rhyzosphere microorganisms, plant cover, plant abundance and Hg bioaccumulation on treated plots. Changes in mercury evaporation (Lumex) and soil respiration (LCpro+ system) related to the plant species were found.

The studies confirmed the possibility of using plants as efficient remediation tools in phytostabilization of mercury-contaminated soil. Mercury volatilization depends strictly on extend of plants coverage and species composition. Soil additives (granular sulfur and zeolites) as soil stabilizers reduced Hg bioaccumulation, volatilization and evaporation.

RO-034

AN EXPERIMENT TO DECREASE METHYLMERCURY EXPORT AND BIOACCUMULATION FROM MANAGED WETLANDS

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Wetlands are critical for wildlife and healthy ecosystem function, and yet are also important areas for methylmercury (MeHg) production, bioaccumulation, and export to adjacent water bodies. Therefore, preserving or restoring wetland habitat, while limiting MeHg export and risk to local food webs, presents a unique challenge to wetland managers. We examined how a combination of wetland design and water management influenced MeHg export and bioaccumulation in order to minimize biological MeHg exposure on-site, and transport downstream. The study area consisted of eight managed wetlands (approximately 10 hectares) that were flooded annually (4-20 cm depth) during mid-September thru late April to provide habitat for winter migratory waterfowl. Four of the wetlands were treatment wetlands, and were constructed with two distinct cells separated with a narrow berm. Eighty percent of the wetland was maintained shallow for water-bird habitat, and the remaining 20% of the area (~2 hectare) at the outflow end was excavated to a depth of ~1 m. The four control wetlands were shallow and relatively uniform in depth. Treatment wetlands were operated in a semi-continuous flow-through mode, while control wetlands were operated in a fill-and-hold mode, where water was only released at the end of the managed flood period. We quantified three MeHg removal mechanisms (particulate settling, benthic demethylation, and photo-demethylation) in the deep-water treatment cells. Over two years, mean whole-water MeHg load (by mass) decreased ~40% from the in-flow to the outflow in the deep cells on average. Photodegradation accounted for ~7% of the mass (18% of loss), while particle flux to the benthos accounted for ~24% (60% of loss) of the MeHg budget. Benthic MeHg degradation was exceeded by MeHg production indicating an unknown loss mechanism accounting for the remaining 9% of the mass (22% of loss) in the MeHg budget. While deep-cells within the treatment wetlands served as net sinks for MeHg, overall the net MeHg export from the flow-through treatment wetlands exceeded export from the fill-and-hold control wetlands. Despite the effectiveness of the deep cell in lowering MeHg export, Hg concentrations in biosentinel fish (Gambusia affinis) showed no change from inlet to outlet. Although the use of deep cells in wetland design were effective in lowering MeHg exports under flow-through conditions, further optimization of wetland management is needed prior to widespread implementation to decrease biotic exposure.

RO-035

AN OVERVIEW OF ACTIVATED CARBON AS A REMEDIATION TOOL FOR MERCURY-CONTAMINATED MARSH SOILS

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In situ Activated Carbon (AC) amendments offer an attractive, potentially low impact approach for reducing contaminant bioavailability in ecologically sensitive environments. Over the last few years, we have carried out several field and laboratory trials to evaluate the efficacy of activated carbon (AC) as a remediation tool for mercury (Hg) contaminated marsh soils. Our focus has been on field trials of thin-layer placement of AC on marsh soils, and on laboratory studies to evaluate the geochemical factors that influence the impact of AC on Hg bioavailability, net MeHg production and MeHg bioavailability. Our studies show that AC can successfully reduce inorganic mercury (Hg) and methylmercury (MeHg) concentrations in porewater, and bioavailability to benthic organisms. However, the effectiveness of AC in reducing Hg and MeHg bioavailability varies among sites and soils. Additionally, AC amendments can change the balance of MeHg production and degradation.

Field trials of thin-layer AC placement have been carried out at the plot scale in three Hg-contaminated tidal locations: a salt marsh in Maine, a Phragmites marsh in, NJ, and a tidal creek bottom in the Chesapeake. Study designs varied, but in all cases, AC amendment plots were compared to untreated control plots, and sediment and pore water biogeochemistry was followed in detail over time. The Maine and NJ plot studies ran for 2 years. We will discuss the efficacy of AC in each of the field studies, in relation to site geochemistry, and over time. We will also present laboratory studies on the impact of sediment chemistry and microbial activity on AC efficacy, and the impact of AC amendments on net MeHg production. Our goal is to develop an empirical model that will allow end-users to evaluate the potential efficacy of AC as a Hg-remediation tool for specific sites. Specifically, we will discuss how soil sulfide and organic matter content impact AC efficacy; the impact of pore water dissolved organic matter on Hg and MeHg partitioning to AC; and the impact of AC on microbial activity and net MeHg production.

RO-036

GEOCHEMICAL CONTROLS ON ACTIVATED CARBON EFFECTIVENESS IN REMEDIATING MERCURY AND METHYLMERCURY-CONTAMINATED SOILS

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In Situ amendments of Activated Carbon (AC) have been used as a low impact method to remediate contaminants in ecologically sensitive environments. Laboratory experiments and field trials have shown that

AC is successful in reducing inorganic mercury (Hg) and methylmercury (MeHg) concentrations in porewater. Yet, the effectiveness of AC varied in different soils, with AC reducing MeHg porewater concentrations between 30% and 90% depending on the soil. These data indicate that site geochemistry might dictate the efficacy of AC use for Hg and MeHg remediation. In the environment, Hg partitioning is effectively a competition between solid phase environmental ligands and dissolved phase ligands. Thus, partitioning can be profoundly affected by high concentrations of ligands, such as dissolved organic matter (DOM) or sulfide. In this study, we evaluated the impact of DOM concentration on MeHg and Hg partitioning to the solid phase in Hg-contaminated sediment/AC mixtures

The experiment was conducted over 21 days in anaerobic sediment/AC slurry microcosms that were amended 5% dry weight AC and Suwannee River Humic Acid at a range of concentrations. Marsh soils were collected from a *Phragmites* marsh in Berry's Creek, NJ. The microcosms were destructively sampled at 5 time points to monitor Hg and MeHg soil:water partitioning (K_D).

Results showed that the addition of SRHA did not significantly impact the partitioning of either ambient MeHg or a fresh $Me^{199}Hg$ spike onto AC. However, DOM did reduce inorganic Hg partitioning (both ambient Hg and fresh ^{201}Hg spike) to AC in soils, in a concentration-dependent manner. DOM is known to slow the formation of HgS nanoparticles, and we hypothesize that DOM impacts the efficacy of AC for inorganic Hg removal in porewater by holding Hg-sulfide species in solution. AC efficacy in MeHg sorption was not impacted by DOM up to 60 mg/L, suggesting that AC may be valuable in reducing MeHg risk even in high DOM soils, like marshes. This study highlights the need to evaluate AC efficacy for remediation in the matrix being considered for treatment and the need to develop models of AC efficacy based on site biogeochemistry.

RO-037

EFFECTIVENESS OF HYPOLIMNETIC OXYGENATION AND CIRCULATION IN EUTROPHIC RESERVOIRS CONTAMINATED BY LARGE-SCALE MERCURY MINING

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The Guadalupe River Watershed in Santa Clara County, California, is contaminated with mercury waste from the former New Almaden Mining District: North America's oldest and most productive mercury mine, and the fifth largest in the world. Though active mining halted by 1970, waste rock and contaminated sediment persist as sources of mercury to the watershed. The Santa Clara Valley Water District (District) manages four water bodies affected by historical mining operations: Almaden, Calero, and Guadalupe reservoirs, and Almaden Lake. These eutrophic water bodies stratify seasonally, creating anoxic conditions that facilitate the bacterial conversion of mercury to bioavailable methylmercury. In 2005, Tetra Tech calculated 5.8 mg Hg/ kg for standardized 40 cm largemouth bass in Guadalupe Reservoir. Signage throughout the watershed warns anglers to not consume fish. The Guadalupe River Watershed Mercury TMDL was adopted in 2008.

Beginning in 2006, the District installed solar-powered circulators in Almaden Lake and hypolimnetic line-diffuser oxygenation systems in the reservoirs to suppress anoxia and methylmercury production. After several years of intermittent operation, continuous operation began in 2016. The effectiveness of the control systems is analyzed using water quality profiles as well as mercury and nutrient samples collected monthly to twice- monthly. Biannually, young largemouth bass and prey fish are sampled and analyzed for mercury body burden.

Results thus far have indicated that Almaden Lake's solar circulators, while failing to improve dissolved oxygen and redox potential, have reduced methylmercury and nutrient concentrations in the water column. The hypolimnetic oxygenation systems in Almaden and Guadalupe reservoirs have improved dissolved oxygen concentrations, leading to decreased methylmercury production and reduced nutrient efflux from bottom sediments. In 2016, seasonal peak hypolimnetic total methylmercury concentrations were reduced compared to pre-oxygenation in Almaden Reservoir from 10.5 ng/L to 1.4 ng/L; in Guadalupe Reservoir from 60 ng/L to 1.3 ng/L; and previously in Calero Reservoir from 13.2 ng/L to 0.46 ng/L (Calero did not efficiently retain added oxygen in 2016). However, epilimnetic methylmercury concentrations increased or were unchanged. Though fish data collected during continuous operation of the oxygenation systems is limited, results have not indicated a decline in fish tissue mercury concentrations. Calero Reservoir, the least contaminated of the reservoirs downstream of New Almaden, exhibited lower fish mercury concentrations than Stevens Creek Reservoir, which is located outside of the watershed and used as a control site. This phenomenon may be due to Calero's larger size, higher algal productivity, and more diverse fish assemblage.

RO-038

NITRATE ADDITION FOR CONTROL OF METHYLMERCURY IN ONONDAGA LAKE, NY: RESULTS FROM A LONG-TERM, WHOLE-LAKE PROGRAM

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The anaerobic sediments of stratified lakes are particularly active zones for methylation of inorganic mercury (Hg^{2+}) and can be an important source of methylmercury (MeHg) to the water column during summer anoxia and fall turnover. Production of MeHg is promoted by anaerobic conditions and the supply of Hg^{2+}, sulfate (SO_4^{2-}), and labile organic carbon. Hg-contaminated Onondaga Lake, NY is naturally SO_4^{2-} rich, and its eutrophic condition contributed an ample supply of organic carbon and low redox potentials. These conditions resulted in accumulations of MeHg in the hypolimnion during the summer stratification interval, followed by entrainment of MeHg into the epilimnion with the approach to fall turnover. Elevated MeHg concentrations during this period represented a potentially important exposure pathway for aquatic organisms.

During 2011–2013, a whole-lake nitrate (NO_3^-) addition pilot test was conducted with the objective of limiting release of MeHg from the pelagic sediments to the hypolimnion through maintenance of NO_3^-–N concentrations >1 mgN/L. A liquid calcium-nitrate ($Ca(NO_3)_2$) solution was added to the hypolimnion from a barge as a neutrally buoyant plume approximately two to three times per week during the summer stratification interval. Water from the surface of the lake was used to dilute the $Ca(NO_3)_2$ solution and achieve neutral buoyancy at 1-2 meters above the sediments. Following a successful pilot study, the program was adopted as part of the long-term remediation program for the lake. The annual dosing of NO_3^- ranged from 5.6×10^4 to 8.8×10^4 kg during the first six years of the program (2011–2016).

Maximum concentrations of MeHg in the hypolimnion remained <0.5 ng/L during the six years of the NO_3^- addition program, a decrease of >94% from 2009 levels. Increased sorption of MeHg to Fe and Mn oxyhydroxides in surficial sediments was identified as an important regulating mechanism. The hypolimnetic NO_3^- supply explained 95% of the interannual variations in hypolimnetic accumulations of MeHg over the 1992–2016 interval. Increased MeHg concentrations in the upper waters during fall turnover, which had been a generally recurring pattern, did not occur during 2011–2016. Lower MeHg concentrations in the water column resulted in lower MeHg concentrations in zooplankton, which in turn may result in lower exposure of fish to MeHg.

RO-039

EFFECTS OF NITRATE ADDITION ON WATER COLUMN METHYLMERCURY IN OCCOQUAN RESERVOIR, VIRGINIA, USA

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This presentation discusses a two year assessment of spatial and temporal patterns of methylmercury (MeHg) and ancillary redox-related constituents (dissolved oxygen, nitrate, iron and manganese) in Occoquan Reservoir, a large run-of-the-river drinking water reservoir in Virginia, USA. A tributary to the reservoir receives input of nitrate-rich tertiary treated wastewater that enhances the oxidant capacity of bottom water and increases the safe water yield of the reservoir. Multiple lines of evidence supported the hypothesis that the presence of nitrate and/or oxygen in bottom water correlated with low MeHg in bottom water by enhancing redox in surfacial sediment. Bottom water MeHg was significantly lower in a nitrate-rich tributary (annual mean of 0.05 ng/L in both 2012 and 2013) compared to a nitrate-poor tributary (annual mean of 0.58 ng/L in 2012 and 0.21 ng/L in 2013). The presence of nitrate and oxygen also corresponded with significantly lower bottom water MeHg at an upstream station in the main reservoir. In 2012 the reservoir exhibited a longitudinal gradient with nitrate and oxygen decreasing and MeHg and manganese increasing downstream. In both study years, there was a clear threshold of oxygen equivalent (3-5 mg/L), a metric that combines the oxidant capacity of nitrate and oxygen, above which MeHg was negligible (< 0.05 ng/L) and Mn and Fe were low (< 0.5 mg/L). The presentation concludes with a comparisons of the relative advantages of using nitrate versus oxygen, another oxidant that can potentially be used to manage redox conditions and mercury cycling in the bottom of reservoirs.

RO-040

IN SITU CONTROL OF METHYLMERCURY PRODUCTION IN SEDIMENTS USING REDOX-BUFFERING MINERAL AMENDMENTS

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Environmental risk from mercury-contaminated sediments derives mainly from methylmercury production, exposure and bioaccumulation. Methylmercury is produced predominantly by heterotrophic sulfate-reducing bacteria. Our research is evaluating the ability of redox-buffering mineral-based amendments to suppress mercury methylation by inhibiting microbial sulfate reduction near the sediment surface, with the objective of reducing methylmercury exposure and food web bioaccumulation. Laboratory sediment-water aquarium microcosms were prepared with homogenized sediment from Nevertouch Marsh in the Berrys Creek Study Area and site water. Manganese(IV) oxide minerals (pyrolusite or birnessite) were either directly mixed into the upper 5 cm of sediment or applied in a thin-layer cap. Overlying water and porewater were monitored. Direct addition of Mn(IV) oxide amendment or inclusion in a thin sand layer resulted in a 66% to 69% reduction in net methylation for pyrolusite and an 81% to 89% reduction for birnessite (measured as %MeHg/THg in porewater at 0 to 5 cm). A thin sand layer alone resulted in 65% reduction in net methylation. CO2 respirometry experiments showed that the amendments stimulated microbial activity. Microbial community census by PCR and DNA sequencing indicated that the addition of Mn(IV) oxides did not significantly alter the indigenous sediment microbial community structure, although a small increase in abundance of iron and manganese reducers was observed after a 2 week incubation period. The

mechanism of methylmercury suppression therefore most likely involved a shift from sulfate reduction to manganese reduction as the energetically favorable redox process, which was also confirmed by microelectrode voltammetry profiling of the sediment microcosms. Manganese X-ray Absorption Spectroscopy (XAS) of amended sediment documented the gradual conversion of Mn(IV) oxide amendments to Mn(III) oxides (bixbyite), mixed-valence Mn(II/III) oxides (hausmannite) and Mn(II)-carbonate (rhodochrosite) and aqueous Mn2+ over time. This solid phase assemblage is expected to continue to buffer redox to inhibit sulfate reduction and suppress mercury methylation in the surficial sediment. The retention of the added manganese in sediment solid phases also has interesting implications for in situ self-regeneration of Mn(IV) oxides in dynamic settings where soils and sediments experience periodic water level and redox fluctuations (e.g. in intertidal zones, tidal marshes, seasonal wetlands, reservoirs), as this would prolong the effective lifetime of the amendments.

4d-2: Technologies and approaches for mitigating mercury emissions

RO-041

POST-MINAMATA ACTIVITIES IN SOUTHEAST ASIA AIMED AT REDUCING MERCURY EMISSIONS

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Several countries in Southeast Asia with sizeable generation capacity installed in existing coal-fired power plants are preparing to implement the Minamata Convention on Mercury. In the process, countries are considering application of best available techniques (BAT) and best environmental practices (BEP) to reduce mercury emissions, as described in United Nations Environment Programmes (UN Environments) draft BAT/BEP Guidance Document, called for in Article 8 of the Convention. This paper presents the various capacity building activities related to BAT/BEP application and carried out by UN Environment in Vietnam and Thailand. The paper also describes results of mercury measurements carried out at coal-fired power plants in the region under a U.S. project in cooperation with UN Environment.

RO-042

NOVEL LDH-DERIVED NIALMO (M=ZN, BA, MN) MIXED OXIDES FOR HG0 ADSORPTION AND OXIDATION IN THE PRESENCE OF NH3

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Simultaneous removal of Hg0 by NH3-SCR catalysts has a profound developing potential. NH3 is the most widely used reductant in low temperature SCR. But it is well known that NH3 exhibited negative effects on Hg0 removal at low temperature because ad-NH3 species prevent Hg0 adsorption. For instance, traditional VWTi catalyst is easily poinsoned by NH3 in Hg0 removal. It is worth mentioning that mixed oxides obtained from hydrotalcite-like compounds exhibit high ecient NH3-SCR activities due to their acid-base character and high surface area, such as MgCuAlO, MgCuFeO, MgAlFeO and MgAlFeCeO.

The hydrotalcite-like NiAlM (M=Zn, Ba, La, Ce, Cr) compounds were synthesized by urea method and calcinated at 773 K. The samples after calcination were denoted as NiAlMO. Before calcination, the XRD pattern of NiAlM precursor shows a hydrotalcite-like structure. After calcination, the hydrotalcite layered structure completely collapsed and only NiO crystalline phases could be observed on all of these samples. It indicated that doping elements might be highly dispersed in the catalyst. The BET surface areas of NiAlBaONiAlZnONiAlMnONiAlLaO and NiAlCrO were 106.01, 110.63, 121.26, 126.44 and 151.48 m2/g, respectively. The result indicated that hydrotalcite-based NiAlM synthesized by urea method indeed had higher specific surface area.

In Hg0-TPD experiments, the amount of Hg0 desorption showed in sequence as: NiAlZnO(125.12mg/g)>NiAlLaO(44.52mg/g)≈NiAlBaO(43.48mg/g)≈NiAlMnO(40.07mg/g)>NiAlCrO(32.81mg/g)>VWTi(11.65mg/g). After introduction of 100ppm NH3, the Hg0 adsorption capacity decreased on all of these samples. But the order of Hg0 adsorption capacity changed as: NiAlZnO(43.89mg/g)≈NiAlBaO(39.44mg/g)> NiAlMnO(31.55mg/g)>NiAlLaO(14.22mg/g)≈NiAlCrO(13.15mg/g)>VWTi(3.32mg/g). Apparently, the performance of the five NiAlMO catalysts was superior to that of VWTi, whether NH3 existed or not. In addition, the desorption peaks of all NiAlMO catalysts were in the range of 100-300°C. When the desorption temperature was higher than 300°C, the effect of NH3 was negligible. It indicated that NH3 mainly affected Hg in the weakly adsorbed state. The large BET surface area may be one of the reasons for the better adsorption performance of Hg0 on NiAlZnO and NiAlMnO. However, the larger surface area of NiAlCrO didn't result in higher Hg0 adsorption capacity. It could be speculated that specific surface area was not the crucial factor for Hg0 absorption.

In summary, the calcined hydrotalcite-based NiAlM, particularly NiAlZnO, NiAlBaO and NiAlMnO have good performance in Hg0 capture even when NH3 exists. It's promising to be used for simultaneous removal of Hg0 and NO at low temperature.

Keywords: hydrotalcite, Hg-TPD, ammonia, urea, manganese

RO-043

IMMOBILIZATION OF ELEMENTAL MERCURY FROM COAL COMBUSTION FLUE GAS BY NOVEL MINERAL SULFIDE SORBENT

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A novel zinc sulfide sorbent with large surface area was successfully synthesized by a liquid-phase precipitation method to immobilize elemental mercury from coal combustion flue gas. Surface area was found to play important role in Hg0 adsorption by zinc sulfide. At relatively high temperatures (140 to 260°C), the Nano-size ZnS (Nano-ZnS) with the largest surface area of 196.1 m2×g-1 exhibited far greater Hg0 adsorption capacity than the conventional bulk ZnS sorbent due to the abundance of surface sulfur sites, which have a high binding affinity for Hg0. The Nano-ZnS Hg0 was first physically adsorbed on the sorbent surface, then reacted with the adjacent surface sulfur to form the most stable mercury compound, HgS, which was confirmed by X-ray photoelectron spectroscopy analysis and a temperature-programmed decomposition test. The optimized temperature for Hg0 removal using Nano-ZnS was 180°C, at which a maximum Hg0 adsorption capacity of 497.84 μg×g-1 was achieved when adsorption bed was 50 % penetrated (inlet Hg0 concentration of 65.0 μg×m-3). Negligible effects of H2O, SO2, HCl on Hg0 adsorption was observed, while NO, especially with the aid of O2, inhibited Hg0 removal by the Nano-ZnS. Compared with several commercial activated carbons used exclusively for gas-phase mercury removal, the Nano-ZnS was superior in both Hg0 adsorption capacity and adsorption rate. With this excellent Hg0 removal performance, non-carbon Nano-ZnS may prove to be an advantageous alternative to activated carbon for Hg0 removal in coal-fired power plants equipped with particulate matter control devices and selective catalytic reduction devices.

RO-044

THE INVESTIGATION OF MOS2 NANOSHEETS FOR HG0 CAPTURE BY MATERIALS GENOME APPROACH

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Compared with graphene, the graphene-like 2D TMDs materials with layered structure exhibit abundant surface chemistry that is importance for adsorption/catalysis processes. There is a great potential for such layered materials decorated with abundant sulphur for mercury capture to address the urgent global challenges. However, the types of TMDs nanosheet and their effects on Hg0 capture remain unexplored. In this research, the Materials Genome approach that integrated computational (stage I), experimental (stage II), and mechanisms (i.e., informatics and data analysis, stage III) study has developed for accelerating discovery of MoS2 nanosheets features for Hg0 capture. Based on computational chemistry simulation results, it is found that MoS2 nanosheets performed the strongest adsorption capability for Hg0 capture. The MoS2 containing adsorbent is then prepared, characterized and evaluated by using various techniques such as XPS, Raman, XRD, HRTEM, NH3-TPD and, in-situ DRIFTS, dynamic transient and steady-state Hg0 capture evaluation in the stage II experimental study. The charge density difference analysis, PDOS analysis and adsorption pathways and energy profiles predictions are further adopted as data informatics tools to reveal the mechanisms of Hg0 captured on the MoS2 surface. The demonstrated materials genome approach in atomic-level shows a great potential for the discovery of nano-materials with defective features as advanced functional environmental remediation materials.

RO-045

STUDY ON MERCURY EMISSION AND MERCURY ADSORPTION CHARACTERISTICS OF FLY ASH AND BIOMASS CHAR IN UTILITY BOILERS

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The mercury emission and adsorption characteristics of fly ash and biomass char were studied in this paper. The mercury emission was obtained by measuring the mercury content in solid samples including coal, limestone, slag, fly ash and gypsum in PC and CFB utility boilers. The relationships were obtained between of the mercury emission and adsorption with physical and chemical characteristics of fly ash and preparation conditions of biomass char. The parameters include unburned carbon content in fly ash, particle size and pore structure, biomass char preparation temperature, heating rate and air. And the mercury adsorption kinetic characteristics of fly ash and biomass char were investigated. The results show that the majority of mercury releases to the atmosphere with the flue gas in PC boiler, while the one is enriched in fly ash and captured by the precipitator in CFB boiler. The coal factor was proposed to characterize the impact of coal property on mercury emissions in this paper. The larger the coal factor is, the lower the mercury emission to the atmosphere is. The results also show that the capacity of adsorbing mercury is directly related to the particle size of fly ash. The mercury content first increases and then decreases with the increase of the particle size in the range of 24.5 to 362.5μm. It is found that the mesoporous content4-6nmis the biggest among 77.5-106μm in the fly ash, which is beneficial to adsorbing the mercury. The pore structure of biomass char influences greatly in physical adsorption. The more cumulative pore volume of biomass char and the more mercury adsorbed. The pores with smaller pore size had better adsorption effect on mercury than those with larger pore size at the early stage of adsorption, while the latter could enhance the total adsorption amount of mercury. The adsorption process was affected by both chemical adsorption and physical absorption, and the former is an important rate-limiting process.

RO-046

DEVELOPMENT OF SELECTIVE SORBENT FOR OXIDIZED MERCURY AND ITS APPLICATION ON SPECIATION MERCURY MEASUREMENT IN COAL FIRED FLUE GAS

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The emission of mercury derived from coal-fired power plant has been brought into global focus for its heavy impact on both environment and human health. Mercury species are difficult to measure accurately in coal-fired flue gas because of their low concentration and distinct physicochemical property. Alkali metal oxides, salts and chlorides efficient selectivity for gaseous oxidized mercury (Hg2+) and are preferred materials for mercury speciation in flue gas. Several novel calcium-based sorbents were manufactured in this study with mesoporous silica support and their features for oxidized mercury selective adsorption were analyzed. By bench-scale fixed bed experiments, calcium-based sorbents mingled with different active ingredients like CaO, KCl, NaOH were compared on their selective efficiency for Hg2+ and anti-interference ability for other flue gas components. Meanwhile, the crystalline structure and surface characteristics are obtained though X-Ray Powder Diffraction (XRD) study, Brunauer-Emmett-Teller (BET) analysis and SEM (Scanning Electron Microscope) analysis. Compared with the original CaO sorbent (C-S), which selectively adsorbed 64.61% of HgCl2 under the simulated flue gas, the composite sorbents (CK-S) mingling CaO with KCl were able to absorb more HgCl2 (85.62%). The surface imperfection formed on CK-S surface during the CaO and KCl eutectic melting process can be responsible for the performance improvement. The increase of oxygen vacancy on CK-S surface effectively enhanced HgCl2 selection and the diffusion of products layer (CaSO4). Furthermore, another calcium-based sorbent labeled as NCK-S was prepared by doping NaOH to CK-S. The selective adsorption efficiency of NCK-S for HgCl2 was up to 95.36%. Actually, NCK-S obtained more basic sites on sorbent surface with the addition of NaOH. Moreover, NaOH can limit CaO dissolutionthrough the common ion effect when the calcium-based sorbents are exposed to moist flue gas. Therefore, NCK-S possessed better sulfur resistance and HgCl2 adsorption capacity than the other two calcium-based sorbents. Finally, the NCK-S along with activated carbons was applied to speciation mercury field sampling on a bench-scale coal-fired unit by EPA Method 30B speciation traps. The gaseous mercury species distribution results by speciation traps coincided to those by Ontario Hydra Method (OHM).

RO-047

STUDY ON THE MERCURY EMISSION AND TRANSFORMATION IN A COAL-FIRED POWER PLANT WITH ULTRA-LOW EMISSION CONTROL DEVICE

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The field test of the mercury emission from the Chinese ultra-low emission coal-fired power plant was investigated by the Ontario Hydro method. Temperature-programmed decomposition desorption, scanning electron microscope and X-ray power diffraction spectrometry were used in this work. Results show that the emitted Hg0 in the stack occupies the largest proportion of the total amount (49.55%) with 16 times of the emitted Hg2+. Mercury in bottom ash occupies the smallest ratio with 0.13%. Hg0 oxidation across SCR (53.26%) plays an important role for the Hg0 removal. HgT removal rate across the APCDs obeys the order of ESP > WFGD > WESP. WESP can further reduce the mercury emission. The emission factor is 1.39 g/1012 J, less than the mean value of Chinese plants. Mercury content in gypsum is higher than the limit while bottom and ESP ash have no effects on the soil. Leaching is not likely but thermal treatment should be paid more attention to the gypsum disposal. Mercury concentration in the WFGD and WESP waste water is higher than the limit, and enough importance should be given on the waste water from WFGD. Mercury transformation mechanism across the power plant is discussed systematically.

RO-048

OPTIMIZING MERCURY CONTROLS IN POWER AND CEMENT PRODUCING PLANTS

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Over the course of its 15 years of industry experience, Ohio Lumex has developed a variety of measurement techniques, products, and services which provide coal-fired utilities and cement kilns with effective means for reducing mercury emissions. The data provided by these measurements has been critical in helping the affected industries minimize operating costs required to meet regulatory limits, via optimization of control technologies and injected materials.

Mercury sorbent traps and portable sorbent trap analyzers allow for quick and reliable on-site and accurate determination of total mercury concentration as well as mercury oxidation ratio, in any sampling environment from the SCR inlet to the stack. Sorbent traps have become the industry standard, and are well-renowned for their self-validation criteria, ease of use, and reliability. In addition to mercury sorbent

traps, Ohio Lumex has designed sorbent traps to measure a variety of common analytes of interest, such as NH3, SO3, HCl, HBr, Se, and As.

Portable mercury speciating monitors yield real-time total and oxidized mercury data, and are designed to function for extended durations in nearly any sampling environment. Permanent mercury monitoring systems are generally installed in stacks or at the inlet to FGDs, and are equipped to send live mercury data directly to the plants data integration system.

Hundreds of engineering studies have utilized these technologies and have demonstrably reduced the cost of mercury abatement via tuning of plant control technologies as well as optimized injection rates of activated carbon, dry sorbents, calcium bromide, sulfides and other materials.

1a-2: Atmospheric mercury cycling and transformations: Insights from measurements and models

RO-049

INCREASING CONCENTRATIONS OF ATMOSPHERIC MERCURY MEASURED IN THE CANADIAN WESTERN SUB-ARCTIC

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The transport and transformation of mercury in the atmosphere has been a topic of discussion in the Arctic for over two decades. While considerable information has been published from Alert, Canada, less has been discussed in Canada's western Arctic. It's been shown that 95% of the anthropogenic Hg deposited in Canada comes from external sources and that ~27% of the anthropogenic mercury deposited in the Canadian Arctic is contributed from Asia. Little Fox Lake, situated in the Yukon Territory in Western Canada, has been identified as a good location to monitor mercury plumes from Asian long range transport into Canada. Since 2007, atmospheric mercury has been measured at Little Fox Lake where annual median concentration levels of total gaseous mercury (TGM) are 1.34 ± 0.15 ng m-3. This annual median concentration is lower than the average Canadian background levels (mean 1.47 ± 0.22 ng m-3). As well, there is a distinct seasonal/monthly median signature in the TGM levels that ranges between 1.18-1.50 ± 0.09 ng m-3). Trends of atmospheric mercury are on the decline in the northern hemisphere and across Canada, but a recent trend analysis from Little Fox Lake (2007-2014) shows a significant increase in the TGM concentration levels in all months but January and February (where the trends were not statistically significant). The MannKendall trend analysis of the Little Fox Lake data showed a monthly median increasing trend of +1.7 ± 0.6% per year (not including January and February) with a range of +0.7 to +2.5% per year. The same trend analysis was performed on data Alert, Nunavut over a similar time period (2007-2013) and showed a monthly median trend of –2.7 ± 1.6 % per year with a range of -7 to-0.8% per year. The increasing trend in the TGM concentration level may be explained by increasing emissions in Asia but also may be a result of regional forest fires or other regional input. An investigation into the atmospheric mercury concentrations at these Arctic locations will be presented.

RO-050

MERCURY EMISSION AND DEPOSITION FROM VOLCANIC SYSTEMS IN CENTRAL AMERICA

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Volcanic systems are a poorly-constrained, natural contributor to the global mercury cycle. Lack of comprehensive data has led to uncertainties in 1) the total amount of mercury emitted from volcanoes; 2) the speciation of mercury upon release from volcanic plumes; and 3) the pathways and timing of deposition following plume release. Three volcanoes (Masaya volcano, Nicaragua; Poas and Turrialba volcanoes, Costa Rica) were studied extensively to determine these uncertainties. These volcanoes represent a diverse variety of magmatic systems within the Central American Volcanic Arc. At each volcanic site, air and soil samples were collected along a distance gradient up to several kilometers downwind from the emission source. Air samples were collected using iodated-carbon traps with a portable pump either by walking through the plume or via drone for the analysis of gaseous and particulate mercury. Soil samples at each site consisted of a depth profile for the analysis of total mercury to establish a timeline of mercury deposition. A suite of aqueous samples was also collected, including rainwater, condensates from a hydrothermal vent, and water from hyper-acidic crater lakes; in situ filtration was used to differentiate dissolved versus particulate mercury. Analysis of the samples was carried out at the Class 100 Ultra-Clean Trace Elements Laboratory (UCTEL) at the University of Manitoba. In addition, real-time atmospheric mercury speciation measurements (gaseous elemental mercury, gaseous oxidized mercury and particulate-bound mercury) were carried out intermittently at locations that are adjacent to Poas and Turrialba volcanos. Preliminary results show that the total gaseous mercury concentrations in the air reach near ambient levels within a short distance from the plume center. Total mercury concentrations in all the water samples are in the order of tens of ng/L. Methylated forms of mercury have also been detected within two volcanic crater lakes and in the condensate from a hydrothermal vent. Analysis of the air trap and soil samples is ongoing. This study represents a comprehensive investigation into the emission and fate of volcanic mercury in Central America.

RO-051

CARIBIC OBSERVATIONS OF MERCURY IN THE UPPER TROPOSPHERE AND LOWER STRATOSPHERE

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A unique set of mercury measurements in the upper troposphere and lower stratosphere (UT/LS) has been obtained during the monthly CARIBIC (www.caribic-atmospheric.com) intercontinental flights between May 2005 and February 2016. The passenger Airbus 340-600 of Lufthansa covered routes to North America, East and South East Asia, and the southern hemisphere. The accompanying measurements of CO, O3, NOy, H2O, aerosols, halocarbons, hydrocarbons, greenhouse gases, and several other parameters as well as backward trajectories enable a detailed analysis of the measurements.

Post-flight processed data since April 2014 provide new insights into the spatiotemporal distribution and speciation of mercury in the UT/LS. We will compare the data with previous observations, estimate the stratospheric mercury lifetime, and discuss a conceptual model of stratospheric mercury cycle.

RO-052

TREND AND SOURCE-RECEPTOR RELATIONSHIP OF ATMOSPHERIC MERCURY OBSERVED AT A TROPICAL MOUNTAIN BACKGROUND SITE IN EAST ASIA IN 2006-2016

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Global inventories suggest increasing anthropogenic atmospheric mercury (Hg) emissions in the past two decades, especially in the East and South Asian regions due to growing industrial activities and energy demands. However, observations at Mauna Loa Observatory and sites in North America and Europe showed decreasing trends in atmospheric Hg concentrations from 1990 to present, inconsistent with current global inventories. Such a trend analysis has not been reported from sites in East Asia due to the lack of long-term monitoring data. Here we reported the trend and source-receptor relationship of atmospheric Hg observed at the Lulin Atmospheric Background Station (LABS), a tropical mountain site in central Taiwan (23.47ºN, 120.87ºE, 2862 m a.s.l.), between 2006 and 2016. Concentration-weighted trajectory (CWT) approach was applied to identify source regions of each atmospheric Hg species, including gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM) and particulate Hg (PHg). Southwest and Southeast China and northern Indochina Peninsula were the common major source regions of all species. For GEM, an additional source region was identified extending from northeast China along the coastal region of east China. Moreover, air from South China Sea and the Pacific Ocean could also be enriched with GOM, possibly due to GEM oxidation. Trend analysis of GEM was performed by using the Sen's slope approach. A significant decreasing trend in GEM concentrations was observed with a rate of -2.1% yr-1 (-0.0336 ng m-3 yr-1) over the 2006-2016 period. This value is similar to those reported from sites in North America and Europe. Further analysis found significant decreasing trend between September and May when LABS is mainly under the influence of air masses from the East Asia continent, but no trend or slightly increasing trend from June to August when marine air masses prevail. Concurrently monitored CO concentrations also showed a significant decreasing trend with a rate of -2.1% yr-1 (-2.904 ppb yr-1) over the same time period. The similar decreasing trends in GEM and CO concentrations suggest that changes in anthropogenic emissions may have played a role. However, other factors, such as changes in re-emission flux, atmospheric chemistry and regional transport pattern, may also contribute. We are still working on detail analysis about the relationships between GEM and other parameters and the trends of GEM concentrations associated with various air mass clusters. Updated results will be reported in the 2017 ICMGP.

RO-053

SPECIATED ATMOSPHERIC MERCURY MEASUREMENTS AT THE MAUNA LOA, HAWAII AMNET SITE: PATTERNS, TRENDS, AND SOURCES

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In January 2011 NOAAs Air Resources Laboratory assumed oversight of speciated atmospheric mercury measurements at the Mauna Loa Observatory (MLO), and the site joined the Atmospheric Mercury Network (AMNet). MLO is one of six NOAA baseline monitoring stations for the study of the background global atmosphere, and is located at an elevation of 3,397 m on the northern slope of the Mauna Loa volcano on the Big Island of Hawaii. A single Tekran speciation system measures

gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM) with nominal 1-hr resolution. Since 2011, measurements of ozone (O3), sulfur dioxide (SO2), and carbon monoxide (CO) were also added.

The site is an ideal high-altitude location from which to monitor the global background atmosphere. Free tropospheric flow at the elevation of MLO is typically from the east and northeast (trade wind circulation), with local upslope/downslope circulation superimposed on the larger-scale flows. Measured mercury species concentrations will be presented with respect to diurnal, seasonal, and annual variations, and trends in mercury concentrations at the site will be discussed. Source regions associated with both high and low mercury concentrations will be investigated through gridded trajectory frequency analysis using NOAAs HYSPLIT model.

Finally, a brief summary of measurement accuracy assessment activities for GOM and PBM will be presented.

RO-054

USE OF CATION EXCHANGE MEMBRANES TO CORRECT GOM LOSS FROM DENUDERS AT THE HIGH ALTITUDE PIC DU MIDI OBSERVATORY

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Gaseous elemental mercury (GEM, Hg) emissions are transformed to divalent reactive Hg (RM) forms throughout the troposphere and stratosphere. RM is often operationally quantified as the sum of particle bound Hg (PBM) and gaseous oxidized Hg (GOM). The measurement of GOM and PBM is challenging and under mounting criticism. Here we intercompare six months of automated GOM and PBM measurements using a Tekran® KCl-coated denuder and quartz regenerable particulate filter (rpf) method with RM collected on cation exchange membranes (CEMs) at the high altitude Pic du Midi Observatory. We find that denuder/rpf sampled RM is systematically lower by a factor of 1.3 than RM on CEMs. We observe a significant relationship between GOM (but not PBM) and Tekran® flush blanks suggesting significant loss (32%) of labile GOM from the denuder or inlet. Adding the flush blank to denuder/rpf based RM results in good agreement with CEM based RM (slope=1.01, r2=0.90) suggesting we can correct bias in denuder/rpf RM and denuder based GOM. We provide a bias corrected (*) Pic du Midi dataset for 2012-2014 that shows GOM* and RM* levels in dry free tropospheric air of 198 and 229 pg m-3 which agree well with in-flight observed RM and with model based GOM and RM estimates.

RO-055

CONTROLLING FACTORS OF MERCURY WET DEPOSITION AND PRECIPITATION CONCENTRATIONS IN UPSTATE NEW YORK

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Observations from the Mercury Deposition Network (MDN) at Huntington Wildlife Forest (HWF) suggested that a significant decline in Hg concentrations in precipitation was linked to Hg emission decreases in the United States, especially in the Northeast and Midwest, and yet Hg wet deposition has remained fairly constant over the past two decades. The present study was aimed to investigate how climatic, terrestrial, and anthropogenic factors had influenced the Hg wet deposition flux in upstate New York (NY). To achieve this, an improved Community Multiscale Air Quality (CMAQ) model was employed, which included state-of-the-art Hg and halogen chemistry mechanisms. A base simulation and three sensitivity simulations were conducted. The base simulation used 2010 meteorology, U.S. EPA NEI 2011, and GEOS-Chem initial and boundary conditions (IC, BC). The three sensitivity runs each changed one condition at the time as follows: 1) NEI 2005 Hg anthropogenic emission out of NYS instead of NEI 2011, 2) 2005 meteorology instead of 2010, and 3) no in-state Hg anthropogenic emission. The study period of all the simulations was March November 2010, and the domain covered the northeastern United States at 12 km resolution. As a result, compared with rural areas in NYS, Hg wet deposition and ambient Hg concentrations in urban areas were affected more significantly by in-state anthropogenic Hg emission. The in-state anthropogenic Hg emissions contributed ~25% of Hg wet deposition at urban sites and <1% at rural sites during the study period. In contrast, the out-of-state anthropogenic Hg emissions had slightly higher (~3%) influence on NYS rural areas compared with urban regions. Using 2005 anthropogenic Hg emissions, around twice of those in 2010, out-of-NYS emissions increased the total in-state Hg wet deposition by 16%. Hg wet deposition flux was greatly affected by meteorological conditions, causing changes varying from a 91% decrease to a factor of 5 increase in monthly accumulated wet deposition amounts. The possible affecting meteorological factors included, not limited to, solar radiation, cloud height, wind speed and direction, precipitation, and relative humidity, among which precipitation had the largest effects in most areas.

RO-056

MODELLING OF ATMOSPHERIC MERCURY IN SOUTH AFRICA

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A modelling study of the emission, transport, transformation and deposition of mercury (Hg) over South Africa has been performed. The study employed a state-of-the-art regional chemical transport model, WRF/Chem with Hg, which is based on the Weather Research and Forecasting (WRF) Model. The study used employed two global anthropogenic emissions databases, two atmospheric mercury oxidation chemistry mechanisms, and different combinations of boundary and initial conditions, in order to gain some insight into the possible level of uncertainty associated with the model output. The model output from all the tested configurations suggest that much of the Hg deposition in some areas of South Africa is due to local emissions, particularly in the Highveld. Hg deposition in other regions of South Africa however is almost totally dominated by long-range transport of Hg from remote sources, in particular the Northern, Western and Eastern Cape provinces. The characteristics of the different climate zones in South Africa, in particular rainfall patterns, all influence the Hg deposition patterns, total depend on deposition fluxes both long-range and local sources, although the relative influence of these sources changes significantly across the country. It proved difficult to reproduce some of the higher gas phase Hg observations, and the reason for this is not immediately clear. It may be due to the time averaged emissions in the model which possibly does not accurately reflect Hg release from industrial installations. It could also be the result of particular meteorological conditions favouring release of Hg from previously contaminated sites. Certainly further investigation is warranted, particularly given the at times significantly high observations (similar to heavily populated and industrialised regions of China), and their unfortunate scarcity. The lack of measurement data for South Africa in general means that it is difficult to make hard and fast comments on the models ability to reproduce atmospheric Hg species concentrations and deposition flux magnitudes. However, the simulations do suggest that most of the Hg released by anthropogenic activities in South Africa is deposited within South African territory, with a lesser fraction transported eastward/south eastward towards the Indian Ocean, potentially influencing Hg deposition in Mozambique and Madagascar.

1c-2: Stable isotope studies of global mercury cycling and bioaccumulation

RO-057

GLOBAL ASSESSMENT OF HG ACCUMULATION IN FRESHWATER FISHERIES USING HG STABLE ISOTOPES

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River and lake subsistence fisheries nourish hundreds of millions of people globally, particularly in nations with high poverty rates. Food security in freshwater fisheries could be undermined by accumulation of mercury (Hg) and other contaminants in these food webs. We find that the mean Hg concentrations in food fishes from freshwater locations in Central Africa, Thailand, Venezuela, and Hawaii exceed limits for safe consumption up to ten-fold, yet have no obvious local source for the elevated levels. The aim of this study is to utilize Hg stable isotopes to interpret source similarities and food chain dynamics that have led to these unusually high Hg concentrations. We compare 12 distinct freshwater communities that support food fishes on four continents. Mercury isotope results demonstrate striking similarities between ecosystems with elevated Hg concentrations in Central Africa and Hawaii, including highly negative δ202Hg and Δ199Hg in fish tissue. These signatures likely arise from terrestrial Hg sources originating from volcanic activity and a lack of photochemical transformations. The lowest mean Hg concentrations in the study were observed in Africa's Lake Tanganyika, one of the world's largest and oldest lakes. Isotopically, Lake Tanganyika also had the highest Δ199Hg and δ202Hg values, which may indicate that photochemical demethylation is an important control on Hg levels in these fish. Although exact source tracking is challenging, significant Δ200Hg indicates that Hg is derived from atmospheric origin for all sites examined in this study. Additionally, preliminary results of different feeding guilds within in each food web show similar δ202Hg signatures after photochemical corrections, signifying that different trophic level organisms are still receiving Hg from a singular source. This study marks the first global use of stable isotopes to examine Hg sources in vastly different food webs, and clarifies patterns of Hg bioaccumulation in freshwater systems that may affect human health and food security.

RO-058

PENGUINS DOCUMENT SOUTHERN LATITUDINAL VARIATIONS OF HG ISOTOPIC SIGNATURES FROM SUBTROPICAL TO ANTARCTIC WATERS

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The extent of Hg contamination in the Southern Ocean ecosystems remains largely unknown and determining its fate and impact in these remote areas involves a major challenge. Seabirds are exposed to large quantities of Hg via their marine food chain and have been identified as effective biomonitors of Hg marine contamination. Penguins, as non-flying seabirds, feed on approximately constant prey and exploit similar foraging habitats during their annual cycle, therefore, they are representative of local Hg contamination. Since they are ubiquist marine birds over the entire Southern Ocean, analyses of their tissues provide information about Hg contamination of the different latitudinal areas. In this work, Hg speciation (GC-ICPMS) and isotopic signatures (CVG-MC-ICPMS) were investigated following non-lethal sampling of feathers and blood in 7 penguin species from the marine environments around the French Southern Ocean territories. These lands cover a wide latitudinal gradient from the Adélie Land (66°39'S, Antarctic) to Crozet Islands (46°25'S, subantarctic) and Amsterdam Island (37°47'S, subtropical). Carbon (δ13C) and nitrogen (δ15N) isotopes were also determined to better understand the food web structure of the penguin species and Hg isotopic information. A good correlation of isotopic signatures between feathers and blood demonstrates that both tissues are valuable bioindicators of Hg local contamination. Mass dependent (MDF) and mass independent (MIF) fractionation signatures obtained in both tissues clearly separated populations geographically, permitting the identification of the distinct ecosystems studied. Feathers of Antarctic penguins displayed lower MDF (δ202Hg) values (0.4-1.0‰) than subantarctic (1.3-2.5‰) and subtropical (2.3-2.7‰) penguins along with increasing southern latitude. For MIF (Δ199 Hg), less variation is observed and most values ranged between 1.3 and 2.3 ‰. These specific isotopic signatures for each penguins population are attributed to different foraging habitats (spatial or depth variations) and different extent of photochemical versus dark demethylation or reduction processes. Overall, this work demonstrates that Hg isotopic variations recorded in penguins' samples provide new information on the major sources of methylmercury (MeHg) in the Southern Ocean ecosystems. For instance, MeHg accumulated in population from subtropical to subantarctic latitude seems to be mainly of marine pelagic origin, while in the Antarctic zone, bioaccumulated MeHg could originate from both coastal and marine waters.

RO-059

STABLE MERCURY ISOTOPE FRACTIONATION IN AEROSOLS AND SNOW IN THE ARCTIC

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Mercury contamination is observed in Arctic food webs despite the absence of significant local Hg point sources, making understanding Hg sources and dynamics in the Arctic an area of active research. It is understood that much of the Hg contamination in the Arctic is a result of long-range transport of atmospheric Hg. Thus, identifying and quantifying different sources is needed to predict how changing sources may affect Hg cycling in the Arctic along with making targeted strategies for mitigation. There is also unique chemistry that occurs in the Arctic that contributes to elevated Hg deposition. In polar spring, atmospheric mercury depletion events occur where gaseous elemental Hg is nearly completely oxidized and deposited to snow. Some fraction is photoreduced back to the atmosphere, which affects the extent these events impact the overall net accumulation of Hg. Stable Hg isotope fractionation can be used to trace, distinguish and potentially quantify various Hg processes. Natural Hg isotopes exhibit a large range in mass-dependent fractionation (MDF) and several types of mass-independent fractionation (MIF). MDF is ubiquitous in nature and occurs during many environmental transformations. In contrast, Hg MIF only occurs during a subset of reactions and is largely produced during photochemical transformations with different reactions displaying different MIF extent and signatures. Odd-mass MIF occurs during aqueous and possibly surficial photochemistry, whereas atmospheric gas-phase MIF occurs for all the isotopes and is reported as even-mass MIF. As part of an exploratory study, stable Hg isotopes in aerosols and snow were measured at Alert in the Arctic spring for years 2011, 2013 2015 to assess the potential of Hg isotopes to help understand and distinguish the various Hg sources and transformations. Preliminary Hg isotope data for aerosols and snow exhibit a large variability in MDF and MIF signatures. The aerosols are characterized by negative odd-mass MIF, which is in contrast to the published data that show mostly positive odd-mass MIF for atmospheric oxidized Hg species. Only three of the aerosol samples display significant even-mass MIF with most aerosols having negligible even-mass MIF. These results also differ from the current published data on atmospheric oxidized Hg species. All snow samples exhibit negative odd mass MIF, consistent with photochemical reduction in surface snow, and show no preservation of even-mass MIF. In addition, aerosol metal and lead isotope data were measured and passive samplers for gaseous Hg were deployed in 2016-2017. Results will be discussed.

RO-060

MERCURY ISOTOPES IN FLYING FISH AS A MONITOR OF PHOTODEMETHYLATION IN THE ATLANTIC AND PACIFIC OCEANS

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Mass independent fractionation (MIF) of Hg isotopes in marine organisms has been used to estimate the relative proportion of monomethylmercury (MeHg) formed in the open ocean that is photochemically degraded prior to entry into the foodweb. Flying fish normally feed in the upper ~10 m of the ocean and a previous study has shown that they contain Hg with the highest level of MIF (Δ199Hg) of all fish in the Northern Pacific open ocean food web. In this study we utilized flying fish as a monitor of the relative photochemical degradation of (MeHg) over large areas of the western Atlantic Ocean (12N to 26S) and the North Central Pacific Ocean (22N to 5N). The Δ199Hg values of the fish range widely between 2.7 and 5.5‰ indicating highly variable proportions of MeHg photodegradation. Based on experimental fractionation experiments and the flying fish Δ199Hg values we estimate that in the surface ocean between 55 and 80% of the MeHg formed is photochemically degraded. The Δ199Hg values do not display a simple relationship with latitude, but do display some spatial patterns. Three processes that may contribute to the observed spatial variability with respect to the amount of photo-demethylation were investigated, including: 1) the average amount of incoming solar radiation (e.g., anglet of solar incidence and cloud cover), 2) light penetration depth (depends on water clarity and is related to chlorophyll content) and 3) the role of dissolved organic carbon (DOC) (acts as complexation agent and photosensitizer). There was no correlation observed between Δ199Hg with solar irradiance satellite data (R2=0.12, p=0.25). In contrast, there is a strong negative correlation between Δ199Hg and satellite chlorophyll concentration (R2=0.67, p<0.001). DOC content was estimated from the MITgcm model and there was a moderate correlation between Δ199Hg (R2=0.43, p=0.015) and DOC. Lastly, we compare variability in Δ199Hg values to methylation and photochemical demethylation rates simulated within a global 3-D ocean circulation model (MITgcm). We find a strong negative correlation between Δ199Hg and each of these rates (R2=0.75, p<0.001 and R2=0.80, p<0.001 respectively). We suggest that the Hg isotopic signature of flying fish is dependent on the environmental conditions and biological processes at specific locations in the oceans and can be used to monitor the extent and mechanism of photochemical degradation of MeHg prior to its entry into marine food webs.

RO-061

CONCENTRATIONS AND ISOTOPIC COMPOSITIONS OF MERCURY IN FOUR TEMPERATE FOREST FOOD WEBS

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Relative to aquatic ecosystems, we have a very limited understanding of the biogeochemical processes of methylmercury (MeHg) in forests. In this study, we examined total mercury (THg) and MeHg and their isotopic compositions in food webs (from basal resources to predatory invertebrates) in four temperate forest ecosystem reserves across the United States, including Coweeta Hydrologic Laboratory in North Carolina (NC), Hubbard Brook Experimental Forest in New Hampshire (NH), University of Michigan Biological Station in Michigan (MI), and Angelo Coast Range Reserve in California (CA). We calculated the trophic biomagnification slope (TMS) of MeHg in forest food webs at each site, and found that the mean TMS values were 0.18 (NC), 0.20 (NH), 0.16 (MI), and 0.24 (CA), which are within the range of TMS values found for freshwater ecosystems (mean=0.16, range from -0.19 to 0.48), implying that biomagnification potential of MeHg is in general similar between freshwater and forest food webs. Stable Hg isotope measurements are still in progress for part of the study, but the isotopic data analyzed so far (n=58) among sites showed a wide range of mass-dependent fractionation (MDF, as d202Hg) ranging from -3.04 to +1.32 ‰ and a smaller range of mass-independent fractionation (MIF, as D199Hg) ranging from -0.44 to +1.72 ‰. When we examined the (incomplete) isotopic data at three forest sites (i.e., NC, NH and CA), we regressed d202Hg or D199Hg against %MeHg in each system and extrapolated to estimate endmember d202Hg and D199Hg of "pure" MeHg. If we assume the starting substrate for MeHg in forest ecosystems is inorganic Hg in the forest floor, the isotopic compositions (as estimated in surface litter samples) in these three sites are quite similar with d202Hg ranging from -2.53 to -1.98 ‰ and D199Hg ranging from -0.41 to -0.31 ‰ (n=7). However, it is intriguing that the estimated "pure" MeHg (based on the available data so far) in these three forests are very different: NC has d202Hg = -0.35 ‰ and D199Hg = +0.32 ‰, NH has d202Hg = +2.50 ‰ and D199Hg = +2.05‰, while CA has d202Hg = +1.15 ‰ and D199Hg = +1.55 ‰. Our preliminary interpretation on this isotopic data is that MeHg, before entering these forest food webs, underwent variable degrees of photodemethylation but it is not yet completely clear what differences in biogeochemical processes among sites leads to the variable d202Hg values of MeHg.

RO-062

ISOTOPIC FRACTIONATION DURING MERCURY RE-EMISSION FROM FOLIAGE:EVIDENCE FOR PLANT UPTAKE FOLLOWED BY PHOTOLYTIC REDUCTION EVIDENCE FOR PLANT UPTAKE FOLLOWED BY PHOTOLYTIC REDUCTION

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The mechanism of mercury (Hg) re-emission from vegetation foliage is currently poorly understood. Here, we systematically applied stable isotope technique to various compartments of a pristine subtropical evergreen forest ecosystem to gain insight into this important process. We observed that the Hg isotope signature of bulk leaf sprout samples from the dominant tree species (10-15 days old; δ202Hg = 0.08±0.74‰, Δ199Hg = −0.20±0.14‰, n=3, ±2σ) was similar in composition to surrounding gaseous Hg (Hg0) in ambient air (δ202Hg= 0.37±0.44‰, Δ199Hg = −0.18±0.04‰, n=9) suggesting that atmospheric Hg0 is a major source of foliar Hg. In relation to sprouts, mature foliage samples (0.5-1.5 years old, n=16) from the dominant tree species were substantially enriched in light Hg isotopes (negative MDF, δ202Hg = −2.82±0.76‰) and slightly depleted in odd mass isotopes (negative MIF, Δ199Hg = −0.32±0.12‰). The large negative δ202Hg-shift (on an average exceeding 3‰) between new and mature leaves is likely caused by kinetic MDF introduced during foliar uptake and air-leaf exchange of Hg0 over time. Furthermore, sunlight-mediated Hg0 gas efflux from intact mature foliage enclosed in a dynamic chamber system exposed to zero Hg air displays δ202Hg in a broad range (−2.47±1.36‰, n=18) that is statistically similar to mature foliage. However, interestingly, most Hg0 efflux samples have a profoundly positive MIF signature (Δ199Hg = 0.17±0.40‰, n=18) in contrast to ambient air and leaf samples. On an average, the Δ199Hg shift between Hg0 efflux and mature foliage Hg runs up to 0.48‰. In-turn, our data support for a temporal evolution towards slightly more negative MIF in mature foliage. The Δ199Hg/Δ201Hg ratio of all foliar samples is 1.06±0.11, which is diagnostically divergent from that of Hg0 efflux data at 0.81±0.06. Unlike leaf uptake of Hg0 with subsequent in vivo oxidation and sorption, processes that presumably trigger diminutive MIF, reduction pathways of Hg2+ bound to reduced sulfur groups in the leaf interior potentially offer an explanation for departing observed (+)MIF in the Hg0 re-emission flux and (−)MIF in the foliage HgII pool after reductive loss. To explain the Δ199Hg/Δ201Hg fractionation trajectory for Hg0 re-emission using existing data in the literature, a mass-balance suggests that maximum 76% of daily Hg re-emission was caused by photo-reduction, and a minimum of 24% by dark/thermal pathways.

RO-063

MERCURY ISOTOPE FRACTIONATION DURING THERMAL- AND PHOTO-INDUCED EMISSION OF HG0 FROM SOIL

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Mercury (Hg0) emission from soil is an important source of atmospheric Hg on a global scale. Soil temperature and solar radiation are the major factors inducing Hg0 emission from soil. We investigated Hg isotope fractionation during thermal- and photo-induced emission of Hg0 from naturally Hg-enriched soils (agricultural and forest soils). Both mass dependent fractionation (MDF) and mass independent fractionation (MIF) were observed. The isotopic composition of emitted Hg0 from the agricultural soil displayed negative δ202Hg (-2.87 to -1.10‰) and positive Δ199Hg values (0.08 to 1.34‰) during both thermal- and photo-induced experiments. The negative shifts in δ202Hg values of emitted Hg0 from agricultural soil relative to reactant soil (δ202Hg = -0.41±0.12‰, Δ199Hg = -0.06‰) were generally larger during thermal-induced experiments (mean = -1.96 ‰) than those during photo-induced experiments (mean = -1.39‰), whereas photo-induced experiments induced larger shifts (mean = 0.68 ‰) in Δ199Hg values than the thermal-induced experiments (mean = 0.21%). The isotopic composition of emitted Hg0 from the forest soil (δ202Hg = -1.17±0.12‰, Δ199Hg = 0.07‰) displayed more negative δ202Hg values (-4.64 to -1.42‰) during both thermal- and photo-induced experiments. Similarly, thermal-induced experiments induced larger positively shifts (mean = -3.32‰) compared to photo-induced experiments (mean = -1.70‰). In contrast to agricultural soil, photo-induced experiments induced smaller shifts (mean = 0.07 ‰) than the thermal-induced experiments (mean = 0.22%). This implies that the organic compounds that affect the MIF of the odd-mass-number Hg isotopes in the presence of light in forest soil were more or less different from that in agricultural soil.

RO-064

ROLE OF PRECIPITATION IN MERCURY ACCUMULATION IN SUBTROPICAL MONTANE FOREST FLOOR: EVIDENCE OF ISOTOPE SIGNATURES

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Wet deposition is an important source of mercury (Hg) input to remote montane forest ecosystems. Although Hg deposition flux through rainfall is typically lower than that from litterfall by a factor of two or more, the contribution of precipitation to biomass production and the associated enhancement on Hg uptake did not receive much attention.

In this study, we characterized Hg, C, N concentrations and their isotope signatures in litter and soil horizons along two slopes of a subtropical montane site (Mt. Ailao) in Southwest China, where the precipitation intensity on the west slope (1200 2650 m) is significantly higher than on the east slope (800-2650 m), to understand the influence of precipitation on Hg accumulation on forest floor. Hg concentration in litter shows little influence by altitude in both slope. However, the concentration in soil exhibits a strong trend with altitude under 2550 m, increasing from 18-216 ng g-1 in west slope and 13-213 ng g-1. At the mountain top, soil Hg concentrations are 60 ng g-1 and 75 ng g-1 on the west and east slope, respectively. Hg input from litter is more important than wet deposition to Hg accumulation on the forest floor, as evidenced by the negative D199Hg found in the surface soil samples (-0.28±0.7‰ in litter vs. -0.37±0.12‰ in surface soil). Hg accumulation in soil can be explained by the increasing rainfall that enhances litter biomass production. Positive d202Hg gradient from 0.5 to 1 ‰ was observed from the litter layer to Oe, Oa and soil horizons at 2100-2650 m altitude on both slopes, while 0 to 0.2 ‰ negative D199Hg-shift was dependent on the density of forest canopy. Principal component analysis of Hg isotopes, C and N data suggests that 88% variations of d202Hg in soil profiles can be explained by the Hg loss during the processes of carbon and nitrogen mineralization, and 70% of D199Hg is caused by the re-emission induced by photoreduction. Significantly higher Hg concentrations and more negative D199Hg in the surface soil on the west slope suggest that precipitation imposes an indirect effect on Hg accumulation by influencing litter biomass production. This study provides new insights in understanding the role of precipitation in Hg accumulation in montane forested areas.

1d-2: Mercury cycling, bioaccumulation and health impacts in polar regions

RO-065

IS CENTRAL ANTARCTICA A SOURCE OF ATMOSPHERIC MERCURY FOR LOWER LATITUDE ECOSYSTEMS?

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The Antarctic plateau ice-covered area of 7 million km2 is a highly photochemically active area during the sunlit period with oxidant concentrations approaching those of tropical or urban mid-latitude environments. Earlier studies carried out on the high-altitude Antarctic plateau with modern instruments also suggested, based on short-term observations (a few weeks) in summer, an intense reactivity of mercury on the plateau at the airsnow interface.

Recent monitoring studies of atmospheric gaseous mercury Hg(0) at Concordia Station revealed the occurrence of multi-day to weeklong depletion events of Hg(0) in ambient air in summer, that are not associated with depletion of O3, and likely result from a stagnation of air masses on the plateau triggering an accumulation of oxidants in the shallow boundary layer. This behavior is radically different from what is usually observed in the Arctic where only mercury depletion events that were associated with O3 depletion (and with a Hg(0)/O3 correlation) have been highlighted so far. Such reactivity was also observed at Dome A, and between Concordia Station and Vostok Station.

According to observations at coastal (or near-coastal) Antarctic stations (DDU, Troll, Neumayer, Terra Nova), the reactivity observed on the plateau in spring and summer is transported on a continental scale by strong katabatic winds. This is well demonstrated by looking at data set of east Antarctica. Hg(II) species can be thus rapidly brought to coastal ecosystems and could provide a source of Hg to coastal and sea-ice organisms. This may explain higher values of Hg that are retrieved in bioindicators, in sea-ice and surface waters. The recent identification of microbial methylation of Hg in Antarctic sea-ice could exacerbate the influence of this atmospheric source for introducing Hg into Southern Ocean ecosystems.

This presentation will give an overview of the functioning of the Hg chemistry in central Antarctica and its potential influence on coastal environments.

RO-066

EXCHANGES OF MERCURY BETWEEN THE SNOW PACK AND ATMOSPHERE AT CONCORDIA STATION ANTARCTICA

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Surface snow samples were collected over three sampling campaigns during the Austral summer from the clean sampling area upwind of Concordia station on the Antarctic plateau. During the first campaign a snow pit was also dug to gain an idea of the stability and temporal profile of mercury in the snow pack in the high Antarctic. In the last campaign (Austral summer 2015-16) a 72 hour experiment was carried out that collected surface snow and precipitation on an hourly basis for comparison with atmospheric measurements to evaluate surface recycling in connection with diurnal solar radiation changes.

Sample analysis was carried out for 202Hg and 79Br using a Thermo Electron Element 2 sector field ICP-MS and an Agilent Technologies 7500cx ICP-MS. Samples were left unacidified for Br, I, Ca, K, Na, and were acidified with 100 µL of ultrapure HCl before mercury analysis.

We conducted three sampling campaigns at Dome C, in the austral summers of 2013-2014, 2014-2015, and 2015-2016, during which snow and atmospheric mercury concentrations (TGM) we measured. The three campaigns had different metereological conditions that heavily affected mercury deposition processes. In the absence of snow deposition (including diamond dust) the surface mercury and atmospheric concentration remained stable without any particular trend. During and after snow deposition, mercury concentrations undergo marked changes. In the 2015-2016 field campaign, several snow deposition events occurred strongly affecting the surface snow Hg abundance. Fresh snow deposits were collected from a bench elevated above ground level to reduce wind blown snow collection, and the concentrations detected (around 100 pg g-1) suggest/confirm the capacity of snow as a mercury atmospheric scavenger. These high concentrations decreased rapidly to 10-20 pg g-1 on average within days of being deposited, influencing the atmospheric TGM concentrations. Apart from this variation, during the high resolution experiment, no diurnal variations in surface snow concentrations ware seen.

Preliminary results from this sampling campaign give us important indications for evaluating mercury cycling on the central Antarctic plateau. The connection between Br and Hg in snow does not show any particular correlation or trend during the high resolution experiment (72h). The connection is more pronounced over time. We found a correlation of R2=0.59 in the snow pit samples. Higher deposition of mercury in surface snow seems connected with an increase in Br suggesting an intrusion of humid air from the coast bringing reactive Br that interacted with mercury.

RO-067

SPECIATION AND BIOACCUMULATION OF MERCURY IN CONTINENTAL SHELF WATERS WEST OF THE ANTARCTIC PENINSULA

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In cooperation with the Long Term Ecological Research (LTER) project along the West Antarctic Peninsula (WAP), this study aims to characterize mercury (Hg) speciation in this region's continental shelf waters and Hg accumulation in the WAP food web. Seawater was sampled using a towfish surface sampler and a trace metal clean rosette at depths of 2 m to 2000 m at northern (64.0-64.9°S), mid-latitude (67.1-68.1°S), and southern (~69°S) stations. In surface waters, total dissolved Hg (THg) and dissolved elemental mercury (DEM) were highest at northern and mid-latitude nearshore stations, but THg at depth was generally higher at mid-latitude and southern stations. Profiles of dissolved total methylated mercury (MeHgT) revealed subsurface maxima in offshore (230 m, 0.61 pM) and coastal (500 m, 0.92 pM) waters at northern stations, while MeHgT at mid-latitude and southern stations (~69°S) was generally lower. At the southern shelf break, MeHgT was highest in 2°C, low O2, Upper Circumpolar Deep Water (UCDW). High unfiltered MeHgT in 1 m sea ice sub-cores relative to surface seawater reveal that sea ice may be an important source of Hg in WAP surface waters for grazers such as the Antarctic Krill Euphausia superba. Accumulation of THg and monomethylmercury (MMHg) was higher in juvenile (7.8 to 20 ng g-1 and 0.7 to 2.9 ng g-1, resp.) than adult (4 to 13 ng g-1 and 0.3 to 1.6 ng g-1, resp.) krill which feed near the coast and under sea ice during overwintering. Nearshore or under sea ice feeding may support MMHg accumulation in E. superba, which was higher in coastal than offshore krill at northern stations over multiple years. Trophic enrichment (~10^2) of mercury was observed between E. superba and feathers of all three Pygoscelis penguins, Adélie (Pygoscelis adeliae), gentoo (P. papua), and chinstrap (P. antarctica) living on neighboring islands to U.S. Antarctic research station Palmer. The mean concentration of Hg in chinstrap (0.77 mg kg-1) was higher than in gentoo (0.15 mg kg-1) or Adélie (0.09 mg kg-1) penguins, likely attributed to higher consumption of krill, specifically juveniles with higher MMHg, suggesting that MMHg may be used as a tracer of food web connectivity in this highly productive, remote marine ecosystem.

RO-068

UNDERSTANDING IN-LAKE VERSUS CATCHMENT CONTROLS ON FISH MERCURY LEVELS IN NORTHERN CANADIAN LAKES

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Leadership and community members in the Dehcho region of the Northwest Territories, Canada, are concerned about mercury concentrations ([Hg]) in food fishes such as Northern Pike (Esox lucius), Walleye (Sander vitreus), and Lake Whitefish (Coregonus clupeaformis). Mercury levels in food fishes vary widely across lakes in a relatively small geographic area, with some lakes having high fish [Hg] and associated consumption advisories. Previous research has been unable to elucidate the main drivers of among-lake differences in fish [Hg] in this region. From 2013-2015, 8 remote Dehcho lakes were sampled for fish, benthic invertebrates, zooplankton, sediment, and water by a collaborative team that included First Nations and academic researchers. Fish mercury concentrations were related to fish stable isotope ratios, age, size, and growth rates, as well as to a suite of water chemistry and sediment variables. Interim results indicate that size-standardized differences in fish [Hg] among lakes were best explained by concentrations of chlorophyll-a for Walleye (R2=0.9), and by dissolved organic carbon concentration (R2=0.6) for Lake Whitefish. For Northern Pike, size-standardized differences in [Hg] were best explained by lake chloride concentrations and age-at-size (R2=0.93). Intercepts of Hg-del15N relationships for each lake were negatively related to pH, and positively related to concentrations of dissolved methyl mercury in water. These results are discussed in the context of causal mechanisms, in-lake versus catchment controls, consumption advice for northern fishers, and a resulting mercury mitigation strategy initiated by the Dehcho First Nations.

RO-069

ARCTOX: A PAN-ARCTIC SAMPLING NETWORK TO TRACK MERCURY CONTAMINATION ACROSS ARCTIC MARINE FOOD WEBS

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Arctic marine ecosystems are threatened by new risks of Hg contamination under the combined effects of climate change and human activities. Rapid change of the cryosphere might for instance release large amounts of Hg trapped in sea-ice, permafrost and terrestrial glaciers over the last decades. Sea-ice disappearance is opening new shipping areas to polluting human industries. The general warming of ocean water masses is expected to affect the cycle of Hg, thereby increasing exposure of marine organisms. Hence, Hg could have high impacts on Arctic organisms, biodiversity and ecosystems and is still a source of major environmental concerns. In that context, providing a large-scale and comprehensive understanding of the Arctic marine food-web contamination is essential tobetter apprehend impacts of anthropogenic activities and climate change on the exposure of Arctic species and humans to Hg. In 2015, an international sampling network (ARCTOX) has been established, allowing the collection seabird samples all around the Arctic. Seabirds are indeed good indicators of Hg contamination of marine food webs at large spatial scale. Gathering researchers from 10 countries, ARCTOX allowed the collection of >5000 samples from twelve seabird species at >40 Arctic sites in 2015 and 2016. These different species have different trophic ecologies (diets and habitats) and will therefore provide information on Hg contamination for the different compartments of Arctic marine ecosystems (i.e benthic, pelagic, epontic, coastal, oceanic). By relying on this new network and by combining Hg analyses with biotelemetry, we aim at (1) monitoring spatio-temporal variations of Hg in Arctic biota. (2) Defining Arctic hotspots of Hg contamination and highlighting sensitive areas that require particular attention and protection. (3) Identifying non-Arctic sources of Hg contamination for migratory Arctic predators.

RO-070

CLIMATE VARIABILITY AND MERCURY LEVELS IN EGGS OF ARCTIC SEABIRDS

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We investigated the influence of climate variability on total mercury concentrations (THg) in eggs of thick-billed murres and northern fulmars from Prince Leopold Island in the Canadian High Arctic. Climate variables were compiled from a variety of ground-based and satellite-derived sources, and included climate data: air temperature, wind speed, sea level pressure, total precipitation, snowfall, rainfall, Arctic Oscillation Index (AO) and North Atlantic Oscillation (NAO) indices; and oceanic data: sea surface temperature, primary productivity, and sea ice concentrations. Mercury monitoring data for the seabird eggs spanned 40 years (1975-2014); and climate influence time lags of 0 to 10 years were evaluated. The main effects of climate variables on THg concentrations were assessed for each time lag using General Linear Models. Models with the most parsimonious fit for both species of seabirds were selected using Akaikes Information Criteria (AIC). The most parsimonious models for northern fulmars included climate variables such as AO, precipitation, and temperature and, for the thick-billed murres, the most parsimonious models included sea ice concentration, precipitation and temperature. Truncated data sets for the past 10 years, when THg concentrations were relatively constant (2005-2014), were reasonably correlated with some climate variables such as precipitation. Overall, the results suggest a small, but significant effect of climate variables on THg concentrations in Arctic seabirds.

RO-071

CONTAMINATION PROFILE AND DISTRIBUTION OF MERCURY IN THE SEDIMENTS OF AN ARCTIC FJORD, NYÅLESUND, SVALBARD

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The presence of mercury (Hg), a transboundary pollutant, is increasing in Arctic region and the Arctic sea may take short time to reflect changes in atmospheric Hg levels. The geochronological and pollution analysis of sedimentary deposits of Arctic fjords can indicate the deposition profile of mercury in this region. The sediment deposit can also explain the environmental changes occurred in the past and will help to understand the present situation as it is influenced by the changes in the glacial inputs. The recent studies have indicated the retreat of glaciers due to climate change and subsequent increase in melt water outflow with high content of sediments. The present study thus focused on the monitoring of mercury content and deposition profile in the sedimentary environment of the Kongsfjorden, an Arctic Fjord in Svalbard. The surface and core sediment samples were collected during Indian Arctic expedition 2014-15 and 2015-16. Mercury concentration was detected by using Cold Vapour Atomic Florescence Spectrophotometer and Direct mercury analyser. Mercury fractionation was also carried out for selected samples. The sedimentation rate in inner Kongsfjorden, Ny-lesund, Svalbard using 210Pb/210Po dating technique was also done. The sedimentation rate ranged between 0.22-0.37 cm/year during the last 112 years. The average sedimentation rate obtained was 0.28 cm/y. The rate has been increased during the last 20 years and it might be due to the increased influx of melt water due to climate change. High variation in mercury deposition was observed. The results showed that mean concentration of THg in sediment was 0.198mg/kg dry weight. The results of fractionation indicated the mobility and bioavailability of mercury in the Kongsfjord sediments. The highest percentage of Hg was in fourth fraction (F4) followed by initial fractions (F2>F1>F3) and final fraction (F5). The high Hg concentration in the initial fractions indicated the availability of mercury for chemical and biological transformations and transport in the Fjord. Hence potential toxic effects are possible in the system.

RO-072

DIFFERING FORAGING STRATEGIES INFLUENCE MERCURY (HG) EXPOSURE IN AN ANTARCTIC PENGUIN COMMUNITY

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Remote regions such as the Antarctic have become increasingly important for investigations into far-reaching anthropogenic impacts on the environment, most recently in regard to the global mercury (Hg) cycle. Pygoscelis penguins are ideal model organisms to track Hg through the Antarctic marine food web as they are long-lived, broadly distributed, and are susceptible to biomagnification due to foraging at relatively high trophic levels. However, using these species as biomonitors requires a solid understanding of the degree of species-specific variation in foraging behaviors act to mediate their dietary exposure to Hg. We combined stomach content analysis along with Hg and stable isotope analyses of eggshell membrane, blood, feathers and common prey items to help explain inter and intra-specific patterns of dietary Hg exposure. Breeding colonies were sampled from four of the major regions of the Antarctic Peninsula to address spatial variation in Hg exposure and diet. In addition, a long-term data set from a single colony where all three species breed sympatrically was used to examine inter-annual variation in Hg and diet. Hg concentrations did not vary significantly among regions of the Antarctic Peninsula and remained fairly consistent over the eight year time period investigated. Hg concentrations did differ significantly among species; Hg concentrations in Chinstrap (Pygoscelis antarctica) penguins were significantly higher than concentrations in Gentoo (P. papua) and Adeli (P. adeliae) penguins. Stable isotope analysis revealed diets of all three species to be dominated by Antarctic krill (Euphausia superba) and to a lesser extent fish. Integrating isotopic approaches with stomach content analysis allowed us to identify species-specific preferences for prey fish insufficiently explained by stable isotope proxies for trophic level. Chinstrap penguins were found to forage on a larger proportion of higher Hg mesopelagic prey fish relative to their congeners targeting epipelagic or benthic prey species. While the potential for adverse effects due to Hg exposure is currently low in Pygoscelis penguins in the Antarctic Peninsula, this approach allowed us to substantiate for the first time, the relatively higher risk of Hg exposure for Chinstrap penguins.

2d-2: Mercury fate in aquatic and terrestrial food webs

RO-073

A FENNOSCANDIAN PLATFORM OF FRESHWATER FISH MERCURY DATA FOR THE EVALUATION OF EFFECTS OF TRANSBOUNDARY AIR POLLUTION

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Fish in freshwater ecosystems constitute an important exposure pathway of Hg to humans and wildlife and thus are considered as critical receptors of long-range transboundary atmospheric transport of mercury (Hg). Fish Hg levels even in remote areas commonly exceed environmental quality standards (EQS) set by the WHO/FAO (0.5 1.0 mg kg-1 ww) and the EQS set by the water framework directive (0.02 mg kg-1 ww) is exceeded in all water bodies across Fennoscandia. Effects of atmospherically transported air pollutants and climate change on fish Hg levels have been studied from a long-term perspective in a Fennoscandian network. We have assembled fish Hg data and associated explanatory variables on fish, climate, deposition and catchment characteristics in a database, through a Nordic cooperation supported by the International Cooperative Programmes on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) and Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM), the bodies under the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP). Individual fish specimen with reported Hg data were retrieved from Swedish (n = 39967), Norwegian (n = 6580), Finnish (n = 19692), and Russian (n = 225) databases. Monitoring of Hg levels in freshwater fish in Fennoscandia has been done since the 1960s, resulting in fish Hg data from a wide range of climatic, depositional, and land cover gradients typical for boreal and subarctic ecosystems. The Fennoscandinavian fish Hg database comprise a variety of fish species (n : perch pike >> i.a, brown trout, arctic char, roach) with a variation in fish species composition within and between lakes. Fish species, size and trophic level is used for the analysis but we also use additional data on water chemistry, climate and deposition to test hypotheses on environmental change on Hg in fish. High Hg levels in fish are usually associated with lakes with high concentrations of dissolved organic matter. Currently, surface waters are browning in boreal and subarctic Nordic ecosystems, possibly impacting Hg levels in fish. However, to understand variation in fish Hg levels many factors that affect Hg cycling and bioaccumulation (e.g., catchment characteristics, water quality, trophic structure, and climate) in addition to atmospheric deposition of Hg come into play. The Fennoscandian database is used to assess effects of long-range transboundary air pollution and climate on Hg in fish, through evaluation of temporal and spatial patterns in fish Hg levels. The results will be communicated to international policy bodies focusing on air pollution and mercury contamination.

RO-074

A “MERCURY ELEVATOR” – A NOVEL VECTOR OF METHYLMERCURY TRANSFER FROM SITES OF METHYLATION TO FISH

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Fisheries in highly productive, nutrient-rich lakes in the Northern Great Plains face Hg consumption advisories. This is counterintuitive since high pH, eutrophic lakes generally have lower fish mercury concentrations than expected based on comparisons to similar sized lakes with lower pH and less productivity. It is well understood that oligotrophic lakes with low pH, high dissolved organic carbon concentrations, and high proportions of wetland area have elevated fish Hg concentrations. Less understood are the environmental factors controlling fish Hg concentrations in eutrophic lakes.

Sources of methylmercury (MeHg) to fish are largely dietary with evidence coming from both experimental and stable isotope studies. Thus, invertebrates are important vectors of Hg from sites of Hg methylation to fish. We investigated the role of Leptodora kindtii (hereafter Leptodora), large (2-14mm), predatory invertebrates, common prey for plaktivorous fish in eutrophic systems, compared to smaller zooplankton, in the trophic transfer of MeHg to fish. Leptodora have been shown to exhibit pronounced size specific diel vertical migration (DVM) in eutrophic lakes where adults remain at or on the sediments by day moving into the water column by night. As a consequence of DVM, adult Leptodora may be an important dietary item for fish feeding in low light conditions common in eutrophic systems, provided planktivores have non-visual means of detecting prey items. We tested the hypothesis that migratory Leptodora act as a vector of MeHg from the sites of methylation to fish communities as an explanation for unexpected high fish Hg concentrations in eutrophic systems.

We measured MeHg concentrations in Leptodora and bulk zooplankton dominated by small copepods collected from a eutrophic prairie lake at mid-morning and mid-night in 20 m of water in 3 m intervals. During the day, the majority of MeHg in water column invertebrates was in the bulk zooplankton in areas less than 9 m deep. However, at depth, the majority of MeHg was in Leptodora. At night, MeHg in the Leptodora pool increased to between 67-96% of MeHg in invertebrates at all depths including shallow regions. Thus, the availability of MeHg in invertebrates in the water column at night was 10X greater than during the day and these invertebrates occupied the entire water column. Since Leptodora are available to fish using mechano-receptive feeding mechanisms, this is consistent with our hypothesis that Leptodora act as a conduit of MeHg from sites of methylation to fish due to upwards migration from sediments at night.

RO-075

MERCURY BIOACCUMULATION IN BIOTA OF THE FINGER LAKES, NEW YORK

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Mercury (Hg) contamination of fish is a global concern due to the deleterious health effects in humans and wildlife associated with ingesting fish with elevated concentrations. This study was conducted to assess Hg concentrations in biota of the Finger Lakes (New York, USA), a region where fisheries are an important economic driver but where no comprehensive assessment of food web Hg dynamics in lakes and streams has been completed to date. This region is of interest for the study of Hg accumulation in biota because the dominant land cover in this region is agriculture, which can affect lake trophic status and thus the bioavailability of methyl Hg (MeHg). Furthermore, there is a point source of Hg in the region from an active coal-fired power plant. The study objectives were 1) to determine if fish Hg concentrations were of concern to human and fish-consuming wildlife, 2) to assess differences in Hg accumulation among lakes and determine predictors of fish Hg concentrations, 3) to evaluate the predictive power of lower trophic level MeHg concentrations on fish Hg concentrations, and 4) to evaluate the influence of dissolved organic carbon and land cover on observed biota Hg accumulation patterns.

Between May October 2015, zooplankton and benthos were sampled monthly in five of the Finger Lakes (Honeoye, Canandaigua, Seneca, Cayuga, and Owasco Lakes). Fish were sampled once over the summer and species targeted from all trophic levels. Two species of stream fish (Blacknose Dace, Rhinichthys atratulus, and Creek Chub, Semotilus atromaculatus) were collected in three tributaries of each lake. Benthic macroinvertebrates representing various feeding groups and periphyton were collected for MeHg determination. Samples for water quality and dissolved organic carbon were also taken in both lakes and streams.

Results for top predatory fish, including Lake Trout (Salvelinus namaycush), Largemouth Bass (Micropterus salmoides), and Walleye (Sander vitreus) showed significant differences among lakes and concentrations above consumption guidelines (300 ng/g wet weight). No clear pattern among lakes was evident in lower trophic level fishes such as Yellow Perch (Perca flavescens) and Golden Shiner (Notemigonus crysoleucas) but concentrations were low. Zooplankton MeHg concentrations varied significantly among months within a lake and among months across all lakes. Lake morphometry, land cover, and water chemistry, including dissolved organic carbon, and lower trophic level MeHg concentrations will be included in a predictive model of fish Hg concentrations.

RO-076

FACTORS AFFECTING MEHG BIOACCUMULATION IN STREAM BIOTA: THE ROLE OF DIET AND DISSOLVED ORGANIC CARBON

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The bioaccumulation of neurotoxic methylmercury (MeHg) in freshwater ecosystems is thought to be mediated in complex ways by carbon (e.g., dissolved organic carbon [DOC]), the forms of mercury (Hg) present, and trophic structure, including the diet composition of heterotrophs. To better understand the combined effects of these factors on Hg bioaccumulation in stream invertebrates and fish, we studied tributaries across a range of DOC and dissolved mercury concentrations in the watershed of Lake Sunapee, New Hampshire, USA. We measured total mercury (THg) and methylmercury (MeHg) in three benthic invertebrate and three fish taxa,. Dissolved THg and MeHg concentrations in streamwater increased linearly with DOC, however, mercury concentrations in fish and invertebrates responded non-linearly to increased DOC, suggesting that MeHg bioavailability may be reduced at high levels of DOC. Methylmercury concentrations in invertebrates increased with trophic position. In addition, fish THg concentrations (and to a lesser extent invertebrate MeHg) increased with increased reliance on autochthonous diet items (as indicated by depleted del13C), suggesting that enhanced Hg bioaccumulation may be associated with a pelagic-based diet. Overall, our results suggest that mercury bioaccumulation in stream food webs is mediated both by streamwater characteristics and trophic structure.

RO-077

FOOD WEB DYNAMICS CONTROL THE FLUX AND FATE OF MERCURY IN AQUATIC AND RIPARIAN FOOD WEBS OF THE COLORADO RIVER, GRAND CANYON

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Mercury contamination is a global issue owing to its long-range transport and toxicity. Variation in Hg accumulation among food webs is well studied, but less attention has been paid to how individual organisms, species traits, and food web interactions affect the movement of Hg within food webs and across ecosystem boundaries. We quantified Hg flux in food webs of the Colorado River in Grand Canyon by coupling measures of animal production, gut content analysis, and Hg concentrations over two years before and after an experimental flood. Mercury fluxes from basal food resources to animals were dominated by consumption of amorphous detritus and diatoms, accounting for ~90% of Hg fluxes among sites and years. Consumption of blackfly larvae was the dominant pathway of Hg flux to fishes, accounting for ~80% of Hg fluxes to fish at all sites. Large spatial and temporal discontinuities in Hg fluxes resulted from among-site differences in animal production and rates of resource consumption, species traits, ecotrophic efficiency (the proportion of total invertebrate production consumed by fishes), and food web stability (the degree to which food webs responded to the flood). For example, pre-flood Hg fluxes to invertebrates in the tailwater section of the river below Glen Canyon Dam were ~50 times higher than fluxes to fish because of a large imbalance between invertebrate secondary production and invertebrate consumption by rainbow trout (the only fish occurring in the tailwater). Invasive New Zealand mudsnails were extremely productive in the tailwater, accounting for 41% of total Hg fluxes to invertebrates, but these predator-resistant taxa were a sink for Hg as they were rarely eaten by trout. The gap between total Hg fluxes to invertebrates and trout narrowed significantly in the tailwater post-flood because mudsnail production declined by 10X, shrinking the pool of Hg that was unavailable to trout. Patterns in Hg flux were much different at downstream sites where food webs were less productive, more complex, more efficient, and more resilient to flood disturbance. Apex predatory fish affected the fate of Hg (moving from river to riparian food webs) by controlling densities of emerging aquatic insects. Food web dynamics affect fluxes of contaminants within food webs and across ecosystem boundaries, and understanding these dynamics is a critical step toward assessing vulnerable populations, managing ecosystems, and mitigating the effects of contaminants in the environment.

RO-078

INFLUENCES ON METHYLMERCURY FATE IN NORTHEAST USA ESTUARIES: INSIGHTS FROM FIELD SAMPLING ACROSS A RANGE OF ENVIRONMENTAL CONDITIONS

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Methylmercury (MeHg) bioaccumulation in estuarine fauna is driven by local and regional scale variables that affect mercury inputs, bioavailability, and trophic transfer. Many of these variables, including organic carbon inputs, water temperature, and salinity, are predicted to change with changing global climate. In order to investigate the influence of these variables on MeHg fate, 12 estuarine sites spanning a range of environmental conditions were sampled during summer 2015. Sites were chosen in Delaware, Connecticut, and Maine in order to span a range of average growing season temperatures. In each region, two sets of paired high and low sediment organic carbon sites were chosen, aiming for one set to have relatively higher salinity than the other. We hypothesized that bioaccumulation would be relatively higher at the sites with warmer growing season temperatures and lower sediment organic carbon. At each of the 12 sites, sediment, surface water, and biotic samples were obtained and analyzed for mercury concentration and appropriate ancillary parameters (e.g. chlorophyll a, dissolved organic carbon, %loss on ignition, etc.). Methylmercury concentration data from both abiotic (sediment, dissolved water fraction, particulate water fraction) and biotic (Menidia menidia, Fundulus heteroclitus, and Palaemonetes sp.) samples will be presented. In addition, conclusions drawn from this and past fieldwork regarding the importance of each variable as a local or regional driver of MeHg fate in Northeast estuaries will be discussed.

RO-079

INFLUENCES OF HABITAT AND SPACE ON ABIOTIC AND BIOTIC MERCURY LEVELS IN ACADIA NATIONAL PARK, MAINE

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Mercury contamination has been documented in Acadia National Park for many decades. The resultant data set of 20 years of studies provides an opportunity to synthesize what we know about mercury in the park. Our objectives were to describe how mercury concentrations vary across space within the park, explain species-level variation in mercury, and quantify how habitat influences the relationship between abiotic and biotic mercury levels. To do this, we created a database of mercury studies in Acadia National Park from published scientific papers, reports, and databases maintained by the park and other organizations. We found sufficient metadata that detailed when and where samples were collected for 675 records of abiotic samples (mercury in surface water) and 1035 records of biotic samples (mercury in blood, feather, egg, muscle, fur, and whole body samples, ranging from invertebrates to eagles). Then we grouped the data by watershed and built two spatially linked statistical models in a Bayesian modeling framework. The first is a model that predicts abiotic mercury using stream- or lakewater pH, dissolved organic carbon (DOC), time of year, watershed, and habitat surrounding the sample site. The second is a model that predicts biotic mercury using the type of sample collected, the species sampled, time of year, watershed, and the surrounding habitat. After fitting the model using Markov chain Monte Carlo sampling, we found that abiotic and biotic mercury were not correlated at the watershed scale. Abiotic mercury levels were strongly correlated with water body chemistry (pH, DOC) and the habitat surrounding each of the samples. Biotic mercury was strongly related to time of year and the type of sample taken, but few species were significantly higher or lower than the mean for all species. Moreover, surrounding habitat did not seem to strongly influence biotic mercury levels. These results suggest that mercury exposure is consistent (and relatively high) across the biota we sampled in the park. The lack of correlation between abiotic and biotic mercury could be due to a lack of connection between some animal mercury exposure and mercury in the surface waters, a mismatch between the spatial scale that the biota represent within their environment, or the scale at which we measured the habitat (e.g., local versus watershed scale). Further, the data document the ubiquity of mercury contamination across the many habitats in Acadia National Park.

RO-080

THE IMPACT OF IMPOUNDMENT: MERCURY BIOACCUMULATION IS ELEVATED IN IMPOUNDMENTS RELATIVE TO FREE-FLOWING SEGMENTS OF A SEMI-ARID RIVER SYSTEM

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Anthropogenic manipulation of aquatic habitats can profoundly alter mercury (Hg) cycling and bioaccumulation. The impoundment of flowing rivers is among the most common habitat manipulations and can result in increased fish Hg concentrations immediately following impoundment. However, differences in Hg concentrations between reservoirs and other habitats are still not well understood at larger spatial scales. We address this question at two scales. First, we evaluated total Hg (THg) concentrations in 64,386 fish from 883 reservoirs and 1,387 lakes located across the western United States and Canada to assess differences between reservoirs and lakes. In a second analysis, we examined differences in Smallmouth Bass (Micropterus dolomieu) THg concentrations between free-flowing and impounded segments of the Snake River in Idaho, USA, a semi-arid river with 22 impoundments constructed between the early 1900's and 1980's along its course. Across western North America, fish THg concentrations were 1.5-fold higher in reservoirs (0.134 ± 0.011 μg/g ww ± standard error) than in natural lakes (0.087 ± 0.006 μg/g ww), though this difference varied among ecoregions. Specifically, fish THg concentrations in reservoirs from the North American Deserts, Northern Forests, and Mediterranean California ecoregions were 1.5- to 2.6-fold higher than in lakes, whereas the two habitats did not differ in four other ecoregions. Along the Snake River, preliminary analyses indicate that Smallmouth Bass THg concentrations in reservoirs (0.141 ± 0.003 μg/g ww) and river segments directly below reservoirs (0.143 ± 0.005 μg/g ww) were 1.7-fold higher than in free-flowing segments not directly below reservoirs (0.082 ± 0.003 μg/g ww). Further, in free-flowing river segments, bass THg concentrations declined with distance from the nearest upstream dam, suggesting that these reservoirs can influence mercury bioaccumulation in fishes far downstream. Possible causes for elevated fish THg concentrations in reservoir habitats could include increased methylmercury production due to thermal stratification, effects of water level fluctuations, or differences in food webs between free-flowing and impounded reaches. Together, these data indicate that elevated fish THg concentrations can persist in reservoirs well past the initial impoundment phase and, coupled with the abundance of impoundments in the west, suggest that reservoirs may play an important role in determining Hg exposure to fish, wildlife, and humans. However, because reservoirs are often heavily managed, they may also provide unique opportunities to mitigate these risks.

2g-3: Legacy site assessment and management

RO-081

APPLICATION OF ADAPTIVE MANAGEMENT FOR MERCURY REMEDIATION IN THE SOUTH RIVER, VA

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Remediation planning, design and construction is underway for the South River and South Fork Shenandoah River in Virginia to address legacy mercury. Mercury was used as a catalyst in manufacturing from 1929 to 1950 at a former DuPont facility in Waynesboro, VA. In the 1970s, a fish consumption advisory was administered, and it remains in effect today. Following investigation, an engineering remedial alternatives analysis and public input, the state selected a Monitored Natural Recovery plan and initiated a monitoring program in 1984. Because mercury levels in tissues of some species of fish were not declining as predicted, the South River Science Team was established in 2001 to understand why fish tissue levels are not decreasing and to evaluate options to address this challenge.

A conceptual model describing the fate and transport of mercury in the South River watershed and possible actions to reduce mercury in fish tissue was developed with input from the South River Science Team. The conceptual model indicates that erosion of bank soils containing legacy mercury is the principle source of loading to the aquatic system. However, due to the size of the river and the complexity of mercury cycling, uncertainties in the conceptual model and the effectiveness of possible remedial actions remain. Moreover, because remedial actions are being constructed on public and private properties, community stakeholders and landowners have questioned the net benefit of the remedial efforts. Remedial designs have been revised to incorporate stakeholder preferences. In order to maximize the likelihood of remedy effectiveness, minimize short-term and long-term risks and address other potential stakeholder concerns, an adaptive management approach to remediation is being implemented.

Adaptive management requires a structured process of prediction, action, monitoring, feedback and adjustment. Based on pre-remedy and post-remedy monitoring, we will show how the initial phase of remediation has achieved the best short-term outcome while reducing technical and social uncertainty via system monitoring and stakeholder feedback.

RO-082

APPLICATION OF A MECHANISTIC MODEL OF MERCURY CYCLING AND BIOACCUMULATION IN THE MERCURY-CONTAMINATED SOUTH RIVER, VA

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Mercury was used as a catalyst in rayon production at a former DuPont facility in Waynesboro, VA from 1929 to 1950. In the 1970s, a fish consumption advisory was established and remains in effect. Fish mercury concentrations have not declined as expected and range from approximately 0.2 to >4 µg/g in 250-300 mm Smallmouth Bass along a 40 km river section downstream of the former rayon facility. DuPont and the Virginia Department of Environmental Quality established the South River Science Team in 2001 to understand why and to evaluate the feasibility of remedial options. Contaminated river banks continue to supply mercury to the river. Total mercury concentrations in surface sediments (0-3 cm) are 10-20 µg/g in some areas. Methylmercury concentrations in surface sediments are above 150 ng/g at some locations. Mechanistic modeling is being carried out to help understand reasons for the slow natural recovery and evaluate the potential effectiveness of remediation options. A mechanistic model of mercury cycling and bioaccumulation in aquatic systems (Dynamic Mercury Cycling Model, D-MCM) was used to simulate 44 km of the contaminated river downstream of the former DuPont facility. The modeled portion of the river was divided into 47 segments ranging in length from 0.5 to 1.1 km. Inorganic Hg(II), elemental mercury and methylmercury were simulated in the water column, sediments and food web. Hydrodynamics, bank erosion, bank leaching, particle transport and key processes in the aquatic mercury cycle were included. Simulations of existing conditions spanned 2006-2014. Model simulations reasonably captured key spatial trends in the contaminated system. Observed and modeled concentrations of total mercury and methylmercury in water, sediments and biota, reached peak levels 5-25 km downstream of the original point source. Ongoing erosion of mercury-contaminated solids from river banks was an important source of continued elevated mercury levels in the simulated system. Predicted and observed concentrations of total mercury and methylmercury in water, sediments, and biota will be presented. Factors predicted to be responsible for spatial and temporal trends at the site will be discussed, as well as the potential benefits of selected remediation options, e.g. stabilizing selected reaches of river banks.

RO-083

DEVELOPMENT AND APPLICATION OF A BIOGEOCHEMICAL REACTION-TRANSPORT MODEL FOR SIMULATING MERCURY METHYLATION IN SEDIMENTS AT TWO MERCURY-IMPACTED SITES IN CALIFORNIA

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Mechanistic computer models that simulate the methylation of mercury in anoxic sediments are an underutilized tool to support remediation measures. Computer models have the advantage of investigating responses of a system to various perturbations, such as different management strategies or the effect of climate change. Application of a mechanism-based model for remediation studies requires building the model using thermodynamic and kinetic constraints and testing its sensitivity to variation of model parameters. A biogeochemical reaction-transport model using the PhreeqC program was modified from prior studies to improve the model description of Hg methylation. Data sets from two mercury-impacted water bodies in California were used to establish a range of values for model input and verify the accuracy of the model response. Rate equations that describe Hg methylation resulting from sulfate or iron reduction were implemented in different ways to compare model response to factors such as sulfate concentration, organic matter, and inorganic mercury (Hg(II)) concentration. The model can take into account the adsorption of Hg(II) to sediments, and dissolution and precipitation of nanosize mercury sulfide to determine Hg(II) concentration. Another parameter that is important but difficult to implement accurately is the model treatment of dissolved organic matter since it can both reduce the bioavailability of Hg(II) through complexation that leads to particles that are too big to pass cell membranes, and it can increase methylation by stimulating bacterial growth. Moreover, the model had to be adapted to the different conditions of the two study sites, since they vary from each other in that one is a managed wetland while the other one is a reservoir impacted by legacy mercury. We compared the model simulations of the two sites as examples demonstrating how to build mechanistic models that can be used to plan remediation measures. For all processes described in the model, a balance between accuracy and practicality had to be found to make the model applicable.

RO-084

APPLICATION OF SWITCHGRASS BIOCHAR FOR MERCURY AND METHYLMERCURY CONTROL IN SEDIMENT UNDER REDUCING CONDITIONS: AN X-RAY ABSORPTION SPECTROSCOPY STUDY

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Elevated concentrations of mercury (Hg) distributed in a range of environmental compartments, including rivers, sediments, lakes, and oceans, are a world-wide concern. A number of remediation methods are available for removing or stabilizing Hg at contaminated sites, including natural attenuation, sediment dredging, soil washing, phytoremediation, and soil and sediment amendments. Here, we investigate the effectiveness of switchgrass biochars (pyrolyzed at 300 and 600°C) as amendments to stabilize Hg under anaerobic conditions. Switchgrass is widely available in North America and can be used to produce biochar at low cost. Microcosm experiments were conducted to evaluate the control of total Hg and methylmercury (MeHg) by mixing Hg-contaminated sediment, biochar and river water under reducing conditions over 600 days. The results indicate aqueous concentrations of total Hg and MeHg were greatly reduced in the presence of biochars over most of the experimental period, with the exception of a spike in MeHg concentration observed at ~440 days in the 600°C biochar system. The aqueous concentrations of Hg were observed to vary over time. Initially, moderate concentrations of Hg were leached from the sediment. With the onset of Fe(III)-reducing conditions, large increases in Hg concentrations were observed, likely due to the release of Hg during reductive dissolution of Fe(III)oxides. As sulfate-reducing conditions were established, aqueous concentrations of Hg declined, likely through the formation of Hg-sulfide phases. The first peak of MeHg concentrations was observed during the onset of Fe(III)- and sulfate-reducing conditions. At late times, methanogenic conditions were established and a second peak of MeHg was observed. Micro-X-ray fluorescence mapping and confocal micro-X-ray fluorescence imaging showed the co-occurrence of Hg with S, Fe, Cu and other elements within or on the surface of biochar particles. Hg LIII edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses indicated that the Hg was present within the biochar particles as Hg-sulfide phases. This study suggests that Hg is bound as stable phases within biochar particles, potentially limiting its rate of transfer back to the aqueous phase and availability for methylation.

RO-085

METHOD OF POPS AND MERCURY CONTAMINATED WASTES DISPOSAL

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Mercury polluted contaminated sites are very serious problems in many countries round the globe. History of industrial area in Neratovice (company Spolana, Czech Republic) started at 1898. Spolana used amalgam electrolysis to produce chlorine since 1948. In sixties, the production of chlorinated pesticides started including components for Agent Orange. In the production of these types of chemicals, a number of employees fell seriously ill and production led to the extensive contamination by dioxins and other persistent organic pollutants.

In 2001, the activities concerning to the decontamination and decommission production building operations contaminated with dioxins and mercury. In August 2002, during the catastrophic floods affecting the lower basin of the Vltava and Elbe Spolana site was inundated by overflowing Labe.

Waste from old amalgam electrolysis Spolana were weighed incinerator SPOVO Ostrava during the years 2010 - 2012. For disposal of these waste the combustion part consists of a rotary kiln and secondary afterburner chamber where the wastes are removed at 1 100-1 200 C, was used. Noncombustible leaving the rest in the form of slag. Providing the necessary combustion temperature during start, operation, and shutdown is achieved by additional gas burners. Secondary afterburner chamber with a retention time of about 2 s to ensure total destruction of highly stable hazardous substances (eg. PCBs, CFCs). Cleaning flue gas - a set of several technics allowing to remove pollutants from flue gases - two-stage wet scrubbing, dioxin filter, DeNOx catalyst.

Wastes were, according to the load mercury content, divided into two groups, namely waste and bulk piece with the different content of mercury.

Overall, therefore, in the material contained an estimated 3 963 kg Hg, 6.5 g of 2,3,7,8-TCDD and about 30 kg of PCB. SPOVO technology without issue warrants listed POPs disposal, if we start from the above it can be assumed that up to around 3 600 kg Hg would be left in the form of vapor into the separator device, which must be captured.

On the basis of the operating parameters of a hazardous waste incinerator SPOVO can assume that the device is completely satisfactory for the decomposition of the material present in the reporting of persistent organic pollutants. Likewise, it is reasonable to assume that the mercury present will largely transferred to the gas phase and its disposal sufficient decides the effectiveness of cleaning of the incinerator. Following these procedures can ensure appropriate disposal of such waste.

RO-086

BIOREMEDIATION OF MERCURY CONTAMINATED MATERIAL USING A BIO-FUNCTIONALIZED SUBSTRATE

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The remediation of mercury (Hg) contaminated terrestrial sites is a challenging area because of the elements mobility and tendency to form toxic compounds which can bio-accumulate. Nature may have provided a remedy. Certain bacteria have the ability to tolerate and disburse Hg from their surroundings using intracellular reduction of Hg2+ cations to elemental Hg (Hg0), which is volatile and disbursed passively in gaseous elemental form (GEM). Enhanced Hg emissions can be readily captured with existing technology. This biological redox reaction is controlled by a mercuric reductase enzyme that is coded for by the merA gene, and using merA carrying bacteria followed by Hg capture and storage may assist in reducing the biogeochemical cycling of this toxic element. Delivery for bio-augmenting sites is challenging considering transport issues for microbial cultures in large volumes, the heterogeneous nature of the terrain, and locations of Hg contaminated sites.

To overcome this delivery issue, this research used a biopolymer to immobilize Pseudomonas veronii, on a solid bulk substrate (zeolite). This bio-functionalized zeolite was dried and stored for several months, then applied to heavily Hg contaminated material. GEM flux from the treated and control material was measured directly using a dual setup of Tekran 2537 ambient mercury analysers using dynamic flux chambers. Oxidised mercury species were also measured using a dual pump set up with CEM filters that were later desorbed and total oxidized Hg content measured using a Tekran 2600 analyser. Two watering regimes were used on both inoculated and control soil trays, 15 and 50 percentv/v, and no nutrients were applied. Bio-functional zeolite was added in a ratio of 50%v/v or 15%w/w. Gaseous elemental mercury flux was measured for a minimum of twelve days post inoculation and three days prior.

Results show a dramatic and distinct spike in GEM emissions after inoculation, with higher emissions under both watering regimes compared to water only and background emissions. A corresponding reduction in gaseous oxidised Hg emissions was noted, as would be expected given the enhanced redox reactions going on. This evidence strongly suggests P.veronii were able to enhance GEM emissions to the point where capture and extraction become viable. Further work is required to optimize the watering and nutrient regime to establish a colony sufficiently self- sustaining such that remediation management requirements are limited, and to establish kinetics parameters.

RO-087

CHEMICAL REDUCTION TO REMOVE MERCURY FROM A HIGHLY ALKALINE RADIOACTIVE WASTE

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Mercury is present in the Liquid Waste System at the Savannah River Site (SRS), a US Department of Energy facility located near Aiken, South Carolina. This system contains legacy radioactive liquid waste that was generated over several decades of nuclear material production in support of the US nuclear stockpile. Historically inorganic mercury nitrate was used as a catalyst to dissolve aluminum assemblies following irradiation. Approximately 60,000 kg of the mercury is present within the approximately 37 million gallons of radioactive waste that is present within this system. The mercury has the potential to impact waste disposal requirements of the final stabilized material.

The liquid waste system uses evaporators to vaporize water from the liquid solution to minimize volume (storage) requirements. Analysis of the feedstock to the evaporators has revealed that the total mercury concentration is 234 mg/L. Mercury present in the soluble fraction (186 mg/L) is distributed between the elemental state (3.46 mg/L), inorganic ionic (50.5 mg/L), and organic (134 mg/L) species. During evaporator operations elemental mercury accumulates and condenses as an immiscible liquid phase that is drained by gravity from the evaporator system. In 2015 over 33-liters of elemental mercury was removed from the liquid waste system during evaporator operations. The removal process for elemental mercury is based upon chemical thermodynamics that dictate the partitioning of elemental mercury between the liquid and vapor phase. This provides one of the most effective purge points for the removal of mercury from the system.

In this investigation chemical reduction and reductive demercuration processes are evaluated as mechanisms to increase the removal of mercury from the evaporator unit operation. The objective is to increase the removal of elemental mercury by converting a fraction of either the ionic or the organic mercury that is present in the system. Non-radioactive waste simulants were used in laboratory scale investigations to determine the effectiveness of various industrial reducing agents in converting the various mercury species that are present in this complex-alkaline solution. The investigation included a selected reductant that is known to facilitate reductive demercuration, an organic mercury removal component that is often coupled with oxymercuration processes used in organic synthesis. Full-scale implementation of the processes within the evaporator unit operation could significantly increase the volume of mercury removed from an existing purge point in the liquid waste system.

RO-088

ADVANCED OXIDATION REACTIONS FOR TRANSFORMATION OF METHYLMERCURY IN ALKALINE SOLUTIONS

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Monomethylmercury and other organomercury species which are present in the Savannah River Site (SRS) Liquid Waste System (LWS) decrease the effectiveness of mercury removal /control systems and increase the leachability of mercury from final wasteforms. An overarching objective of ongoing SRS LWS mercury activities is removal of mercury from the LWS at a rate that would reduce overall mercury mass in the system over time thus making operations sustainable as the entire radioactive waste inventory is processed into final stabilized forms (primarily high level waste glass canisters and a cementitious saltstone). An emerging strategy to help meet this objective is deployment of technology to alter mercury speciation within the LWS to control mercury behavior. Advanced oxidation processes, such as photoreactions and ozone reactions, have the potential to break down methylmercury into ionic and elemental mercury forms. In this speciation-control example, conversion of organomercury to inorganic ionic mercury or elemental mercury would measurably improve saltstone performance and would provide a purge point for mercury from the LWS an existing high-quality environmentally-protective wasteform.

As a scoping step, the mechanisms and rates for the conversion of methylmercury to inorganic mercury species by advanced oxidation processes were evaluated/quantified. Two technology classes were studied, photooxidation with UVC wavelength light and oxidation by ozone. All phases of the research emphasized conditions that are applicable to the complex chemistry of alkaline liquid waste solutions/simulants. The work was performed in several phases: 1) preparation of methylmercury simulants/solutions, 2) determination of the optical properties of the simulants/solutions, 3) development of rapid mercury speciation methods, 4) photoreactor tests, and 5) ozone tests. The research confirmed that advanced oxidation techniques, particularly photoreactions, are capable of converting monomethylmercury into inorganic mercury species such as inorganic ionic mercury and elemental mercury (along with other more recalcitrant mercury species). The rate of reactions was relatively slow, particularly in the complex redox chemistry of alkaline LWS simulants which contain a number of metals and high levels of nitrate/nitrite. The data suggest that developing effective oxidation processes will be a challenge and that such processes are likely to result in significant collateral impacts on the chemistry and flowsheet for the LWS.

4d-3: Technologies and approaches for mitigating mercury emissions

RO-089

OVERVIEW ON MERCURY CONTROL OPTIONS FOR COAL-BURNING POWER PLANTS

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With the USEPA issuing a national regulation requiring a minimum of 91% removal of mercury, the need exists for low-cost mercury removal techniques that can be applied to coal-burning power plants. The injection of powdered activated carbon into the ductwork upstream of the particulate control device is the most developed technology for mercury capture. Alternative techniques for mercury capture will also play a role in the near future because of the numerous configurations of air pollution control devices present within the power plants, as well as the many different coals being burned. These methods employ sorbents, catalysts, scrubber liquors, flue gas or coal additives, combustion modification, flue gas cooling, barrier discharges, and ultraviolet radiation for the removal of mercury from flue gas streams. The DOE Mercury Program has been a huge success, spurring continuing development, demonstration, and commercialization of many technologies for the capture of mercury.

An overview of current and alternative technologies for mercury capture from coal-derived flue gas will be provided. In addition, six patent/patent pending methods for mercury as well as carbon dioxide control within coal-derived flue and fuel gases have been recently developed at NETL, and will be discussed. The on-going research needs for mercury control include improved sorbent-flue gas contact, development of poison-resistant sorbents and catalysts, novel sorbent promoters, new scrubber additives for retention of mercury within wet FGD systems, concrete-friendly activated carbons, new continuous measurement methods, byproducts research, development of an ASTM standard lab test for sorbent activity for mercury capture, and exploration of international markets.

RO-090

MONITORING GASEOUS MERCURY WITH A PRECISE, ACCURATE AND INEXPENSIVE PASSIVE SAMPLER

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Our recently introduced passive air sampler for gaseous mercury (Hg) uses a radial diffusive barrier to control uptake kinetics and sulfur-impregnated activated carbon as a sorbent. An initial outdoor calibration in Toronto revealed highly linear uptake over a one-year period and unprecedented precision. The accuracy of this sampler depends on the extent (i) of the variability of its sampling rate SR (i.e. the volume of air stripped of mercury per unit of time) between different deployment locations and periods, and (ii) to which it will be possible to account for that variability. We addressed this issue two-fold. On the one hand, we measured uptake in passive samplers deployed for up to one year at 22 locations with ongoing active sampling for mercury around the world. The sites in Canada, USA, Australia, China, Germany and Taiwan varied widely in terms of climate (tropical to polar regions) and concentration levels. On the other hand, we quantified in the laboratory how the SR varies with tightly controlled temperature, wind speed and relative humidity. The results in either case confirm that the SR of the sampler varies only to a minor extent and the variability is predictable. When accounting for this variability, the sampler can discriminate even very small concentration differences on the order of 0.2 ng/m3. Successful early applications of the new sampler include (i) the detailed characterization of the spatial and temporal variability of Hg concentration around a major known source, which allows for long term exposure assessment of the local population and for the estimation of a Hg emission rate, (ii) the identification of unknown Hg emission sources within a large urban conglomeration, and (iii) the reliable quantification of the isotopic signature of atmospheric Hg.

RO-091

FABRICATION OF SILVER NANO-PARTICLES FUNCTIONALIZED ADSORBENTS FOR HG0 ADSORPTION

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Mercury, emitted from coal-fired power plant, is a serious threat to human beings. Mercury from combustion flue gas commonly displays three chemical forms: elemental (Hg0), particulate-bound (Hgp) and oxidized (Hg2+) form. Despite that the oxidized (Hg2+) and particulate-bound (Hgp) mercury can be relatively easily captured by conventional pollution control facilities, it is more challenging to remove Hg0 than other forms of mercury because of its insolubility in water and weak interaction on conventional adsorbent particles.

To suppress the emissions of the mercury in flue gas, especially for the removal of Hg0. Various novel adsorbents based on silver nanoparticles (NPs) functionalized materials, including zeolite derived from fly ash (ZFA), garphene oxide (GO), and mesoporous silica (SBA-15) were prepared by facile chemical methods. And the mercury cold vapour atomic fluorescence spectrophotometry (CVAFS) was applied to explore the mercury adsorption capacity on the adsorbents. The functionalized materials were successfully synthesized and well characterized. Ag NPs were found to be homogeneously deposited on all the substrates. All the adsorbents demonstrate excellent Hg0 adsorption capacity and fast Hg0 adsorption rate at medium and low temperature. Moreover, our adsorbents show excellent cyclic performance. Certain adsorbents could be reused for at least five successive adsorption-desorption cycles without any significant loss in adsorption performance, providing great advantages in practical applications. Our study clearly indicated that our silver NPs functionalized materials could be used as potential adsorbents for mercury emission control in coal-fired power plant.

RO-092

NANOSENSORS FROM SUSTAINABLE PROCESSES TO SUPPORT MITIGATION OF MERCURY CONTAMINATION RESULTING FROM ILLEGAL MINING IN COLOMBIA

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Afro-Colombians inhabitingPacific rural regions of Colombia havebuilt their subsistence economy onfarming, fishing, and chemical-free artisanal mining. Recently, illegal, small-scale gold mining is increasing in these Pacific rural regions.Many affected rural communities suffer from public health issues and environmental degradationas a result ofirresponsible use ofmercuryamalgamate during mining.Bio-accumulation of mercury potentiallyleads todevastating public health problems onthe nervous, immune, and digestive system for affected local community members. The goal of this project was to developa low-cost portable nanosensor that was durable enough for field use in a variety of applications.To accomplish this, we have developeda laser inscribed grapheneelectrode on a biodegradable polymer for under $1 per electrode. We metalized the graphene electrode with nanometals,such ascopper and platinum andtested for detection of ionic mercury using anodic stripping voltammetry. Theresults show thequantitative limit of detection in lake water was 11.1 ppb, and we are testing other nanometal structures with the aim of measuring Hg2+ as low as 1 ppb (4.5 nM). The response time of the sensor is less than 5 min, and the range extends to 1000 ppb.We are currently comparing the nanoplatinum-graphene sensor to the nanocopper-graphene sensor to create the most effective sensor for thesecommunities.The future work aims to develop methods incorporating metal from waste and to recycle the polymer in an effort to minimize the environmental footprint of the work and extend the sensor to other communities in need of quick detection formercury. These sensors will be used to create mercury heat maps of the local region, providing critical high resolution datasets that will be used to develop public health risk analysis models.

RO-093

REMOVAL OF GASEOUS MERCURY CHLORIDE BY A MODIFIED ACTIVATED CARBON

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The properties of surface oxygen-containing functional groups (SOFG) on activated carbons was investigated, and their effects on removal of gaseous mercury chloride (HgCl2) was studied. For this purpose, the surface of a coal-based commercial activated carbon BPL was modified by heating in an inert atmosphere and then impregnated with benzoic acid solution. Afterwards, all carbonaceous samples were tested for their HgCl2 adsorption capacities. Nitrogen (N2) adsorption, Fourier Transform Infrared Spectroscopy (FT-IR) and Boehm titration were applied to study the surface characteristics of carbon samples. It was found that after benzoic acid impregnation, the amounts of SOFG improved with the increasing of benzoic acid concentration, especially carboxylic and carbonyl groups. Adsorption experiments showed that higher HgCl2 adsorption capacities were obtained with more carboxyl and carbonyl groups. And the largest capacity obtained in this study was 484.7 lg/g of carbon with carboxyl and carbonyl concentrations of 0.570 mmol/g and 0.706 mmol/g, respectively. This suggests that carboxylic and carbonyl groups play predominant roles in HgCl2 removal. And carboxylic groups are believed to contribute more than that of carbonyl groups in HgCl2 capture process.

RO-094

MAGNETIC SBA-15 SUPPORTED SILVER NANOCOMPOSITES AS NOVEL REGENERABLE SORBENTS FOR HG0 REMOVAL FROM FLUE GAS

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Mercury pollution from flue gas of coal-fired power plants has attracted worldwide attention in recent years, and elemental mercury (Hg0) is the most challenging form to be removed and often escapes into the atmosphere directly. In this work, a new class of regenerable magnetically responsive nanocomposites is synthesized by a novel, yet simple and robust approach for efficient Hg0 capture. The sorbents (denoted as MagS-Ag) are composed of silica film-coated magnetite Fe3O4, mesoporous silica SBA-15 and supported silver nanoparticles. Each component has a specially designed function. The silica-coated Fe3O4 makes the sorbents easily separated from fly ash for further recovery and regeneration. SBA-15 is a potential scaffold loading highly disperse and small-sized silver nanoparticles due to extremely high specific surface areas, highly uniform mesopores and favorable mass transfer performance. On the basis of well-known amalgamation mechanism, the silver nanoparticles can effectively capture Hg0 at lower temperatures and release it at higher temperatures accordingly. The physical and chemical properties of MagS-Ag sorbents were investigated by various characterization methods. In Hg0 breakthough tests, a complete Hg0 capture by MagS-Ag was achieved at 150°C, which reflects the typical real flue gas temperature. The sorbents were found to possess a Hg0 capture capacity as high as 5.2 mg·g-1 when the Hg0 breakthrough reached only 1%, extremely higher than present Ag-based sorbents and even comparable with some modified activated carbons. In addition, MagS-Ag were able to achieve a 90.4% Hg0 removal efficiency and 226.1 μg·g-1 capacity when exposed to more stringent flue gas flow for 1 hour with a space velocity of 260,000 h-1. More importantly, the spent sorbents could be effectively regenerated and reused multiple times without any performance degradation. The excellent Hg0 removal capability in combination of facile synthesis, strong tolerance to complicated flue gas, superior thermal stability, and outstanding separation and regeneration performance makes MagS-Ag promising magnetically responsive sorbents for practical application in Hg0 capture from coal-fired flue gas.

RO-095

DFT STUDY OF HG COOPERATIVE OXIDATION CATALYZED BY V2O5/TIO2 DURING DENITRIFICATION PROCESS

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Chinese coal-fired plants are now commonly equipped with SCR catalyst for NOx removal. Through injecting NH3, it will catalyze the NO reduce to N2. Many researchers have found the cooperative effect of SCR catalyst on Hg0 oxidation. The SCR catalyst will facilitate the Hg0 oxidized by HCl and O2 during the denitrification process. Some researchers have also established the oxidation mechanisms of Hg0 using experiment and DFT calculation. The mechanisms consistently reflect the fundamental effect of HCl on the Hg0 oxidation. However, before SCR catalyst, NH3 will be injected into the flue gas to reduce NOx. NH3 and NO will play important role in Hg0 process.

NH3 has been certified by experiment as a prohibitive factor on Hg oxidation. Both promotion and prohibition effect of NO on Hg oxidation have been reported in experiment tests. However, the most likely cooperative removal mechanisms have not been fully determined now.

In this paper, quantum chemistry calculation based on density functional theory (DFT) was applied to reveal the influence of NH3, NO on Hg0 oxidization catalyzed by V2O5/TiO2. Firstly, the related V2O5/TiO2 surface model was established. Secondly, the of reduction of NOx and NH3 was calculated. Next, The oxidization of Hg0 under SCR surface was established. Finally, reaction path was established between denitrification and Hg0 oxidization on V2O5/TiO2 catalyst process. Experimental data obtained from previous studies was used to validate some of the simulation results as well.

RO-096

MIGRATION AND EMISSION CHARACTERISTICS OF HG IN COAL-FIRED POWER PLANT OF CHINA WITH ULTRA LOW EMISSION AIR POLLUTION CONTROL DEVICES

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The emission and migration characteristics of Hg from an ultra low emission (ULE) coal-fired power plant in China was investigated. The flue gas was sampled simultaneously at the inlet and outlet of selective catalytic reduction (SCR) system, low temperature economizer (LTE), electrostatic precipitators (ESP), wet flue gas desulfurization (WFGD), and wet electrostatic precipitators (WESP) by EPA 30B method. The feed coal, lime, limestone slurry, process water, fly ash, bottom ash, gypsum, FGD effluent, and WESP effluent were also sampled. The results showed that Hg concentration in flue gas at the outlet of boilers and stacks was in the range of 4.46-5.17μg/m3 and 0.51-1.22 μg/m3, respectively. The overall gaseous Hg removal efficiencies of existing air pollution control devices (APCDs) ranged from 88.5% to 89.6%. About 41.43%-51.61% of Hg0 was oxidized across SCR systems, and most of Hgp and Hg2+ was captured by ESP and WFGD, respectively. The LTE could significantly affect the distribution and speciation of Hg. The WESP could result in the oxidation of Hg0, which could enhance the removal of Hg. Mass distribution of Hg in the whole system showed that about 70% of Hg present in solid and liquid combustion products and 30% of Hg emitted into atmosphere. The atmospheric emission factor of the power plant before ULE reformation is in the range of 2.18-2.34 g/TJ, which are decreased dramatically to 0.39-0.81 g/TJ after ULE reformation. Thus, the ULE reformation for coal-fired plants is beneficial for the reduction of Hg emission to atmosphere.

1a-3: Atmospheric mercury cycling and transformations: Insights from measurements and models

FO-001

GLOBAL DISTRIBUTION OF MICROBIAL GENES INVOLVED IN THE HG CYCLE IN THE ATMOSPHERE

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Microorganisms play a fundamental role in the mercury cycle on a global scale. In both terrestrial and aquatic environments, microorganisms modify Hg speciation and thereby change the contamination potential of Hg. Bacteria are able to magnify the toxicity of this compound via the methylation of inorganic forms of Hg (Jensen and Jernelv, Nature 1969) and they can act as detoxifiers through the reduction of divalent Hg species with the mer operon (Hamlett et al., J. Bacteriol 1992). The atmosphere is an important route for transporting Hg over long distances and is also where Hg is converted into soluble, labile species that are likely to interact with microorganisms. Yet, atmospheric studies tend to disregard the role of airborne microorganisms in the transformation of Hg species. Only recently have studies shown that up to 105 microbial cells can inhabit one cubic meter of air and that they might be metabolically active in the atmosphere (Klein et al., Front Microbiol 2016). Given the potential for microbial activity in the atmosphere coupled with the different forms of mercury, microorganisms might be transforming mercury in the atmosphere. INHALE (Investigation of tHe Atmosphere as a reaL Ecosystem, ANR) is one of the first projects to assess the Hg-microbial interaction in the atmosphere and to determine the potential role of airborne microorganisms in altering the speciation of Hg and its contamination potential at a global scale. We investigated air samples taken from several high altitude sites around the world involved in Hg geochemical cycling investigations. Hg cycling gene quantification was carried out following atmospheric DNA extraction from filters to assess the presence and abundance of these genes in the atmosphere. The global distribution of the genetic determinants involved in biological Hg cycling in atmospheric microbial communities was then determined. Based on these preliminary results, we proposed a potential role for airborne microorganisms in Hg transformations in the atmosphere. This atmospheric microbial activity may explain changes in Hg speciation and toxicity and help us to understand its potential impact on ecosystem and human health, and to improve global Hg cycling models.

FO-002

TOWARDS MOLECULAR-LEVEL UNDERSTANDING OF THE ATMOSPHERIC MERCURY CHEMISTRY

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Vast quantities of gaseous elemental mercury (GEM) are released to the atmosphere by fossil fuel combustion and waste incineration. The oxidation and precipitation of atmospheric GEM are principal processes governing the transfer of mercury to the ocean and soil environments. Molecular mechanisms of GEM transformation to gaseous oxidized mercury (GOM) and subsequent removal of GOM by surfaces are poorly understood. On the basis of recent experimental, field, and modeling studies, the reaction of GEM with atomic bromine has been suggested as the first step in GOM formation. We will present our work focused on the development of a flow reactor chemical ionization mass spectrometry approach for investigation of gas-phase and gas-surface reaction mechanisms of GEM and GOM. The implications of our work towards understanding of complete mercury oxidation mechanism and achieving chemically-resolved detection GOM in the atmosphere will be discussed.

FO-003

ATMOSPHERIC MERCURY MODELING: COMPARISON OF LAGRANGIAN, EULERIAN, AND HYBRID METHODOLOGIES

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The NOAA HYSPLIT-Hg model has been applied to simulate the fate and transport of mercury emitted to the atmosphere using Lagrangian (i.e., plume-oriented), Eulerian (i.e., gridded), and hybrid Lagrangian/Eulerian simulation methodologies. The hybrid approach has been implemented in several ways, but essentially utilizes a Lagrangian methodology to simulate local and regional fate/transport and an Eulerian framework at further distances from a given source. In each case, the model has been used to estimate: (a) the wet and dry deposition to selected receptors (e.g., the Laurentian Great Lakes), and (b) source-attribution for this deposition, including the relative importance of anthropogenic vs. other emissions sources, and among anthropogenic sources, the relative importance of different countrys emissions. In addition, concentrations and deposition at selected measurement sites e.g., Beltsville (Maryland, USA), Grand Bay (Mississippi, USA), and Mauna Loa (Hawaii, USA) have been estimated by the model and compared with observations at the sites. There are numerous computational and other tradeoffs among the different approaches. The different computational fate and transport frameworks can, in principle, yield equivalent results, if each was able to accurately capture all relevant phenomena. In practice, each has a number of limitations and inherent uncertainties. Further, uncertainties in emissions, atmospheric chemistry, and deposition processes can manifest differently in modeling using the different frameworks. All of these factors lead to variations in simulation results. Differences in deposition and source attribution results for key receptors are sometimes found among the different methodologies, as well as variations in the estimated concentrations and deposition at measurement sites. The relative importance of these discrepancies in different cases will be presented and discussed, along with estimates of the relative contributions of different computational factors to the dissimilarities found. These results provide useful insights into uncertainties in atmospheric mercury modeling due to the characterization of dispersion phenomena. Where the modeling results are compared with ambient measurements, the results show the relative ability of the different approaches -- in the cases and conditions studied to reproduce spatial, temporal, and chemical variations in observed mercury concentrations and deposition.

FO-004

WHAT MODELERS MAY NEED TO ADD TO MECHANISMS OF GLOBAL OXIDATION OF GASEOUS ELEMENTAL MERCURY INITIATED BY BROMINE

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Goodsite et al. (2004) published the first mechanism for the Br-initiated oxidation of gaseous elemental mercury (Hg(0), aka GEM). Their mechanism considered BrHg radical reacting with OH or Br to form HgBr2 and BrHgOH as stable Hg(II) species (gaseous oxidized mercury, GOM). In 2012, Dibble et al. used quantum chemistry to verify the stability of a number of BrHgY species (Y=NO2, HOO, BrO, ClO). We noted that these radicals, Y, should react with BrHg with rate constants similar to those of BrHg + Br. Since these radicals, Y, are much more abundant than Br or OH, reaction of BrHg with Y should dominate over reaction with Br and OH throughout most of the atmosphere. Recent kinetic studies in our group confirm the high rate constant for BrHg reacting with NO2 and HOO to make BrHgONO and BrHgOOH.

Unfortunately for modelers, there is a great deal of additional chemistry that will likely need to be added to mechanisms of Br-initiated oxidation of mercury:

a) Near ground level, except in polar regions, BrHg tends to fall apart to Br + Hg before it can react with radicals. However, we find that BrHg may react with alkenes. As alkenes are much more abundant than radicals, reaction of BrHg with alkenes could enable efficient conversion of GEM to GOM. This would be of particular importance in the marine boundary layer influenced by continental air. We are computing rate constants for the reactions of BrHg with alkenes and will investigate the fate of the resulting radicals.

b) Recent findings suggest that BrHgONO will rapidly (~1 hour) photolyze to form BrHgO. Our results to date indicate that BrHgO will abstract hydrogen atoms from organic compounds in the gaseous atmosphere to form BrHgOH. Ironically, this was the major product of GEM oxidation in models based on the work of Goodsite et al. Competing reactions of BrHgO can lead to BrHgONO2 or regenerate BrHgONO.

These results point to significant interactions of oxidation pathways of atmospheric mercury with trace organic compounds. We hope that these results are incorporated into models and support the development of methods to identify Hg(II) compounds in the atmosphere.

FO-005

WET AND DRY DEPOSITION OF TOTAL MERCURY AND METHYLMERCURY AT AN UNPOLLUTED SITE IN PUERTO RICO

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Wet deposition of mercury (Hg) at an unpolluted site in windward northeastern Puerto Rico is comparable to the highest levels in the continental USA. Here we update the existing seven-year record after two years of measurements at a relocated station, provide estimates of dry Hg deposition based on throughfall and litterfall, and quantify methylmercury (MeHg) in wet and dry deposition. In 2006-2007 (the most complete record), annual wet Hg deposition averaged 27.9 g m-2. High deposition is attributed to scouring of global pool Hg from the upper free troposphere by rain near the tops of high convective clouds, as well as high rainfall amounts (2855 mm y-1). After years of logistical difficulty operating the station at a remote ridgetop tower, we relocated the station 11 km west to a NADP site in August 2014. This station has less rainfall due to its lower elevation (360 vs. 480 m) and the measurements coincided with a significant drought in 2015. Wet Hg deposition in calendar year 2015 was 14.3 g m-2 with 1777 mm rainfall. Weighted average Hg concentration decreased from 9.8 ng L-1 at the original site to 8.0 ng L-1 at the new site, perhaps because the drought was most intense during the summer months when rainfall Hg concentrations are typically highest. Preliminary wet and dry deposition measurements did not overlap well in time and space, but indicate that dry Hg deposition is important. For calendar year 2014, litterfall Hg deposition (representing primarily dry deposition of Hg0) at the NADP site was 38.0 g m-2. Throughfall Hg deposition (representing primarily dry deposition of Hg2+) for 9 months of overlapping measurements at the original site in 2006-2007 was 54% greater than wet Hg deposition. The percentage total Hg as MeHg was 0.06 % in rainfall, 0.56% in throughfall, and 0.31% in litterfall. Combined, these measurements suggest that dry Hg deposition is considerably greater than wet, and that relative input of (or conversion to) MeHg in the forest canopy is considerably less than published values.

FO-006

EMISSIONS FROM BIOMASS BURNING: A MODELLING ASSESSMENT OF THE PARTICULATE-PHASE MERCURY IMPACT ON DEPOSITIONS OVER LAND AND OCEANS

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Biomass Burning (BB) is an important source of mercury (Hg) in the atmosphere. A largest fraction of this Hg is released in the form of elemental Hg, however there are many experimental evidences that an important fraction (up to the 30%) is released bounded to particulate matter (PBM). The exact mechanisms and factors that control emission and speciation are highly uncertain. Indeed, Hg speciation is one of the most important factors affecting Hg deposition and the ratio local/non-local contribution. This work was aimed to investigate the speciation process during BB and its impact on Hg deposition by using the Global Fire Emissions Database (GFEDv4.1s) included into a global Hg chemistry transport model. Results showed that quantity and the geographical distribution of Hg species emitted by BB has a limited impact on a global scale. On the other hand, this impact is remarkable at local scale on those ecosystems close to the BB process. One of the most important consequence is the reduction of the Hg fraction amount deriving from BB, which deposits to the worlds oceans (from 71% to 62%). In addition, results of the model were compared with measurement made within GMOS network. Inclusion into the model of PBM released by BB showed a better agreement between modeled and observed PBM concentrations at remote sites. In light of the Minamata Convention and the progressive decline of Hg emissions from anthropogenic activities, this work shows the growing impact of BB contribution on Hg deposition.

FO-007

REASSESSMENT OF MERCURY EMISSION OUTFLOW FROM CHINA AND EAST ASIA

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East Asia is the largest emission region of anthropogenic mercury (Hg) in the world, with China as the biggest emitter. There have been concerns regarding the transport budget of mercury in the region. Earlier assessments of transport budget are based on relatively outdated emission estimates, which does not represent the regional emission appropriately. Since then, new estimates on anthropogenic (Wu et al., 2016, doi: 10.1021/acs.est.6b04308) and natural emissions (Wang et al., 2016, ACP, doi:10.5194/acp-16-11125-2016) in the region show substantial different from earlier estimate. Most notably, anthropogenic Hg emission in China gradually decreased since 2011 due to better emission control, with a much larger fraction of oxidized mercury than previously thought (56/43/3 for Hg0/HgII/Hgp in 2014). The natural release of elemental mercury vapor from soil, vegetation and water surfaces using new soil Hg data in China and updated model schemes shows a distinct spatial distribution of estimated mercury release compared to the previous estimate (Shetty et al., 2008, doi:10.1016/j.atmosenv.2008.08.026), despite a similar net natural release at ~460 Mg y-1 in China. Such a spatial distribution transition also has an impact on regional model results. In this study, we applied the updated Hg emission estimates to reassess the regional transport budget using CMAQ-Hg v5.1. The emission differences are compared and the model results detailing the emission, deposition and air Hg enrichment are presented. Total Hg deposition in East Asia is 746 Mg yr-1 (422 Mg yr-1 in China). Given the changes in anthropogenic emission, speciation and natural emissions spatial distribution, the transport budget in the East Asia region is 25% lower (631 Mg yr-1) than the previous estimate by Lin et al. (835 Mg yr-1, doi:10.5194/acp-10-1853-2010). The greater Hg mass accumulated within the regional domain also better explains the elevated atmospheric Hg concentrations observed in China recently. At least 60% of Hg deposition in China is caused by local anthropogenic emissions. The overall transport budget in China is 505 Mg yr-1, 55% of which is contributed by natural Hg emission. The Hg emission outflow from East Asia can contribute to 10-15% of Hg deposition in other regions of the world.

FO-008

SOURCES AND THUNDERSTORM EFFECTS ON MERCURY AND TRACE METAL WET DEPOSITION ALONG THE NORTHERN GULF OF MEXICO

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Continuous event-based rainfall samples were collected at three sites throughout the Pensacola airshed from 2005 - 2011. Samples were analyzed for total mercury (Hg), a suite of trace metals (TMs), and major ions to understand atmospheric Hg transport and estimate the contribution from regional coal-combustion on Hg wet deposition. Our findings show that summertime Hg rain concentrations are higher compared to other months despite higher rainfall amounts. In contrast, other measured pollutant TMs or ions did not show a consistent seasonal pattern. By incorporating Automated Surface Observing System data from nearby Pensacola Airport and WSR-88D (Nexrad) data from Eglin Air Force Base, we are able to classify the storm type (thunderstorms or non-thunderstorms) and analyze altitudes of hydrometeor formation for individual rain events. This showed that mid-altitude and high-altitude composite reflectivity Nexrad values were higher for both thunderstorm and non-thunderstorm warm season (May Sept) rain events compared to cool season (Oct Apr) events including cool season thunderstorms. Thus, warm season events can scavenge more soluble reactive gaseous Hg from the free troposphere. Two separate multiple linear regression analyses were conducted on log-transformed data using interaction and non-interaction terms to understand the relationship between precipitation depth, season, and storm-type on sample concentrations. The regressions without interaction terms showed that the washout coefficients for more volatile TMs like Hg and selenium were less pronounced compared to other pollution-type elements and were therefore less diluted for a given increase in precipitation depth, but otherwise displayed similar coefficients for season and storm-type. The regression analysis with interaction terms revealed a more interesting dynamic where thunderstorms caused enhanced rainfall Hg concentrations regardless of season while causing increased dilution for all other TMs compared to non-thunderstorm samples for a given precipitation depth. However, concentrations increased during thunderstorms for all non-Hg TMs with increasing sample depth. This suggests a vacuum cleaner effect was occurring such that for increasing storm strength, non-Hg aerosol TMs in the boundary layer are further entrained into a storm cell. With this understanding, a positive matrix factorization (PMF) analysis was conducted using the EPA PMF 5.0 software to estimate the contribution of different sources to Hg deposition. Preliminary results suggest that approximately 81% (71 92%; 95% CI) of Hg wet deposition along the northern Gulf of Mexico is due to long-range sources while 17% (0 18%; 95% CI) comes from regional coal-combustion.

2d-3: Mercury fate in aquatic and terrestrial food webs

FO-009

MERCURY BIOMAGNIFICATION IN AQUATIC FOOD WEBS ON A GLOBAL SCALE

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Mercury (Hg) concentrations in aquatic organisms of a food web increase with trophic level (TL) through a process called biomagnification. The trophic magnification factor (TMF) metric using the slope of the relationship between Hg concentration and TL (measured using ratios of stable isotopes of nitrogen; d15N) is generally used to quantify biomagnification. TMFs can be compared among systems to understand drivers of biomagnification. TMF averages approximately 8 times increase of Hg concentrations per trophic level (times/TL) for methyl Hg, but ranges from 1 to 64 times/TL across diverse food webs on a global scale. Based on an analysis of 69 food web studies conducted between 1992 and 2013 in marine and freshwater systems across the globe, we previously showed that some of this variation is related to latitude, with Arctic food webs having higher TMFs (~10 times/TL) than those from the tropics (~4 times/TL). Higher biomagnification in colder food webs is believed to be the result of slower growth rate leading to accrued bioaccumulation. Also, areas with high Hg inputs (via atmospheric deposition) tend to have food webs that exhibit lower trophic magnification of this metal, thus lessening risk from exposure in these otherwise contaminated food webs. However, much of the variation in TMFs across aquatic systems remains unexplained. Here we revisit and add TMF and ancillary (e.g., pH) data to this global dataset to further explore patterns and drivers. We identified an additional 74 studies completed between 2013 and 2017 for potential inclusion in the existing database. These include studies on under-represented systems such as hydroelectric reservoirs that are known to result in high Hg concentrations in predatory fishes after dam construction. In addition, we assess whether variations in bioenergetics and food web dynamics could explain variations in TMF. Given ongoing Hg emissions, deposition and transformations, understanding Hg behavior in food webs at a global scale allows for critical links to be made between system characteristics and top predators in food webs that can be used to identify areas at greatest risk from legacy inputs or those that may respond more quickly to global reductions in Hg emissions.

FO-010

RECOVERY OF AQUATIC INSECT-MEDIATED METHYLMERCURY FLUX FROM PONDS FOLLOWING DRYING DISTURBANCE

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Small ponds exist across a permanence gradient and pond permanence is hypothesized to be a primary determinant of insect community structure and insect-mediated methylmercury (MeHg) flux from ponds to the surrounding terrestrial landscape. Here we present the first experiment examining the recovery of insect-mediated MeHg flux following a drying disturbance that converted permanent ponds with insectivorous fish to semi-permanent ponds without fish. We used floating emergence traps to collect emergent insects for 10 weeks in the spring and summer from five ponds with fish (permanent) and five ponds that were drained to remove fish, dried and refilled with water (semi-permanent). Methylmercury flux from dragonflies (Odonata: Anisoptera) and phantom midges (Diptera: Chaoboridae) was significantly greater from newly refilled semi-permanent ponds than permanent ponds but the other eight taxa did not differ between treatments. Beginning 11 days after semi-permanent ponds were refilled, total MeHg flux from semi-permanent ponds was never significantly less than permanent ponds, indicating that insect-mediated MeHg flux had rapidly recovered in semi-permanent ponds following the drying disturbance. The present study demonstrates the impact of an ecological factor like drying disturbance on the cross-system transport of contaminants from aquatic to terrestrial ecosystems.

FO-011

MERCURY AND STABLE ISOTOPES OF NITROGEN REVEAL AN AQUATIC DIET FOR SEVEN TAXA OF SHORELINE SPIDERS

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Mercury (Hg) is a hazardous aquatic contaminant that can be transferred from the aquatic to the terrestrial environment via emerging aquatic insects. Spiders transfer Hg to terrestrial consumers such as birds, but how spiders become contaminated with Hg is not well understood. In the present study, we used stable isotopes of nitrogen (δ15N) in combination with total Hg (THg) to determine the source of Hg to seven taxa of shoreline spiders. We collected orb weavers (Araneidae), wolf spiders (Lycosidae), long-jawed orb weavers (Tetragnathidae), lynx spiders (Oxyopidae), fishing spiders (Pisauridae), jumping spiders (Salticidae), and crab spiders (Thomisidae) along with a variety of aquatic and terrestrial plant, invertebrate, and vertebrate samples from 10 experimental ponds located in north Texas, USA. Orb weavers, long-jawed orb weavers and fishing spiders were the most strongly connected to the aquatic food web and had the highest concentrations of THg. However, δ15N and THg values suggest that all taxa of shoreline spiders examined in the present study consume aquatic organisms.

FO-012

PATTERNS OF MERCURY AND ORGANIC CO-CONTAMINANTS IN MARINE AND FRESHWATER FISH

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Fish consumption advisories have been established throughout the US for freshwater and coastal ecosystems. Most of the fish consumption advisories in the US are for mercury (81%), but significant numbers of others have been established for organic contaminants including PCBs and their congeners, chlordane, DDT, and others. Although the

advisories are contaminant specific, humans are exposed to multiple contaminants through fish consumption. Past studies have focused only on individual contaminants, in particular mercury, without relating those exposures to others such as organic contaminants. Using publicly available datasets in which multiple contaminants were measured in individual fish and invertebrate samples, we examined the relationships between different contaminants (metals, pesticides, PCBs, PAHs, and PFCs) from the EPAs Environmental Monitoring and Assessment Program (EMAP) in lakes, National Coastal Condition Assessment (NCCA), National Rivers and Streams Assessment (NRSA), and the Mussel Watch Program. Preliminary results indicate species-specific relationships between contaminants and some general differences between freshwater species and marine species. Across datasets, Hg in fish and invertebrate tissue correlates both positively and negatively with PCBs, DDT formulations, and some pesticides (e.g., dieldrin, aldrin, chlordane). Correlations of Hg with organic contaminants appear to be mostly negative in rivers and lakes but positive in coastal waters. We examined the co-occurrence of mercury and organic contaminants in fish from a range of ecosystems in order to begin to evaluate the risk of human exposure to multiple contaminants posed by eating seafood and understand the processes related to their co-occurance in aquatic organisms.

FO-013

SYSTEMATIC REVIEW OF TRENDS IN FISH TISSUE MERCURY CONCENTRATIONS

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Since the 1970s there has been a major international effort to monitor mercury (Hg) concentrations in fish tissue to identify areas with fish Hg concentrations that are of concern to human health and wildlife. More recently, numerous data sets, based on these monitoring programs, have been compiled and used to evaluate trends in mercury in fish from both freshwater and marine systems. We reviewed the academic literature and published government reports that assessed temporal trends in fish or invertebrate tissue mercury concentrations. Our goals were to summarize the overall trend patterns in fish tissue Hg concentrations, and to review and evaluate the statistical methods used for trend assessment.

We identified more than 180 papers published between 2005 and 2015. Together, these papers reported on the analysis of over 1,050,000 tissue samples from at least 17,000 sampling sites. In many cases, these studies compared fish Hg data to Hg emissions and deposition data to assess the effects of local controls on Hg emissions as well as the influence of global atmospheric Hg emissions. We summarized and catalogued the results of the trend analyses by waterbody type, species, and geographic location, and by the direction (increase/decrease) and magnitude of trends. Generally, the results of the published studies are equivocal. The direction and magnitude of significant trends in fish tissue Hg concentrations vary by region and are not always consistent with trends in atmospheric emissions. In some analyses, where consistent trends have been identified in a geographic area, the results indicate that the fish Hg levels either declined or remained stable between 1970 and 1990 during the period of the largest reductions in mercury emissions. Numerous studies show no trend or an increasing trend in fish tissue concentrations between 1995 and 2012.

During the course of the review, information on the influence of other factors that affect the relationship between atmospheric Hg deposition and tissue Hg levels was recorded. These factors include temperature effects and food web structure. The statistical methods used in the reviewed trend analyses are summarized with the goal of providing information to optimize future sampling and analysis efforts.

FO-014

EFFECTS OF POND PERMANENCE AND SEASON ON ODONATE-MEDIATED MERCURY FLUX AND ASSOCIATED RISK TO NESTLING RED-WINGED BLACKBIRDS

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In the U.S. Great Plains, millions of human-made ponds have been contaminated with mercury (Hg) deposited from the atmosphere. Methylmercury (MeHg) can be transferred from these ponds to terrestrial predators by emergent aquatic insects. The effects of pond permanence and season on insect-mediated MeHg flux from ponds have not been well studied. Small human-made ponds exist across a permanence gradient from permanent, that always contain water and fish, to temporary, that dry periodically and are fishless. The presence of fish reduces the population sizes of odonate taxa (damselflies and dragonflies) and could therefore reduce odonate-mediated MeHg flux from permanent ponds. We examined the effects of pond permanence and season on odonate-mediated MeHg flux in experimental ponds and its potential risk to nestling red-winged blackbirds (Agelaius phoeniceus), an odonate predator. Exuviae of emergent odonates were collected from emergence platforms in permanent ponds with bluegill (Lepomis macrochirus) (n = 5) and temporary ponds without fish (n = 5) over an eight-month period (January August, 2015). Methylmercury flux was computed by multiplying the number of exuvia collected on emergence platforms by the biomass of adult odonates and the average MeHg concentration of adult odonates captured in floating-emergence traps. Fish predation reduced odonate-mediated MeHg flux by suppressing emergence of damseflies and aeshnid and libellulid dragonflies. Emergence of damselflies, aeshnid dragonflies and libellulid dragonflies peaked in April, May, and June, respectively, and overlapped with reproduction of red-winged blackbirds. We calculated odonate-based wildlife values (the minimum odonate MeHg concentrations causing physiologically significant doses in consumers) to assess exposure risks for three sizes (0.004, 0.02 and 0.04 kg) of nestling red-winged blackbirds with diets consisting of a low (40%) and high (90%) percentage of odonates. Methylmercury concentrations in odonates exceeded wildlife values for all three sizes of nestlings with both low- and high-odonate diets. The present study suggests that MeHg concentrations in odonates can pose a threat to small-bodied nestling birds that consume large amounts of odonates. This MeHg threat to songbirds may extend throughout the U.S. Great Plains.

FO-015

SPANNING THE (ECOSYSTEM) GAP: AQUATIC INVERTEBRATES SUBSIDIZE NUTRIENTS AND MERCURY TO TERRESTRIAL RIPARIAN SONGBIRDS IN LENTIC AND LOTIC HABITATS OF THE WILLAMETTE RIVER, OREGON

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Aquatic and terrestrial food webs are intrinsically linked through cross-ecosystem subsidies of nutrients. Despite the importance of cross-ecosystem nutrient subsidies for ecological function, bioaccumulative and harmful contaminants, such as mercury (Hg), also follow these subsidies through energy pathways. The flux of Hg out of aquatic systems may cause deleterious impacts to terrestrial species that rely on aquatic subsidies. Riparian songbirds, in particular, are sensitive to Hg effects and can be heavily dependent on the flux of emergent aquatic insects for prey sources during the breeding season. In this study, we elucidated the relationship between carbon and Hg movement from aquatic to terrestrial ecosystems along the Willamette River in western Oregon, a water body with a legacy of Hg pollution from gold and Hg mining in its headwaters. The Willamette River, though now largely channelized, was historically made up of a series of braided channels. The legacy of this braided system is found in backwater lentic habitats with varying degrees of connection to the main stem lotic habitats. These lentic habitats serve an integral conservation role for fish, flood control, and riparian habitat, but also may facilitate higher Hg methylation rates.

This study quantifies MeHg and carbon-13 isotope in terrestrial and aquatic invertebrate communities in both lentic and lotic systems of the Willamette River. In 2013, riparian songbird blood samples (N = 480) and baseline aquatic and terrestrial invertebrate (non-predators and predators) were collected at 12 sites (7 lotic and 5 lentic). We then compared MeHg and carbon signatures in the base of the food web with THg and carbon-13 in blood samples from riparian songbirds. Our preliminary findings indicated that terrestrial and aquatic non-predatory invertebrates differ in both Hg and carbon-13 signature, when accounting for site, date, and invertebrate family. Non-predatory aquatic insects in lentic habitats had higher Hg concentrations than in lotic habitats, but no there was no difference in Hg between terrestrial invertebrates living near lentic or lotic habitats. Predatory invertebrates in terrestrial habitats showed Hg bioaccumulation and carbon signatures that suggest a reliance on aquatic-based nutrients. Preliminary data suggest that birds that forage on more aquatic based carbon (based on carbon-13 isotope) also showed higher levels of Hg in their blood.

FO-016

MERCURY EXPOSURE OF BREEDING LEACH'S STORM-PETRELS RELATED TO THEIR FORAGING HABITATS IN THE NORTHWEST ATLANTIC OCEAN

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Leach's storm-petrels (Oceanodroma leucorhoa = Hydrobates leucorhous) are small seabirds that breed on coastal islands and make long, multi-day foraging trips during incubation, often beyond the continental shelf. We are working to assess the role of mercury as a stressor on breeding populations of this bird, which are declining at many breeding colonies in Atlantic Canada. In 2013-15, we attached geolocator tags to adult storm-petrels at seven breeding colonies in Atlantic Canada, to monitor their foraging trips during incubation. When the birds were recaptured 2-4 weeks later, the geolocator data were downloaded and a small blood sample was collected for analysis of total mercury and stable carbon and nitrogen isotope ratios (δ13C and δ15N). Leach's storm-petrels made offshore foraging trips that averaged 4.3 days in length, covered 1,481 km in total distance, and foraged over ocean depths ranging 44 – 5700 m. Mean mercury concentrations (± SE) in Leach's storm-petrel blood (n=193) were significantly greater from four colonies around Newfoundland (Baccalieu 1.11 ± 0.05 µg/g, Gull 1.00 ± 0.06 µg/g, Middle Lawn 1.28 ± 0.09 µg/g, and Grand Colombier Islands 1.27 ± 0.05 µg/g) than from three colonies in the Gulf of Maine (Bon Portage 0.65 ± 0.08 µg/g, Kent 0.57 ± 0.04 µg/g, and Machias Seal Islands 0.37 ± 0.06 µg/g). Blood mercury concentrations were positively related to the depth of the ocean over which birds foraged and to the distance that they foraged away from their breeding colonies, and were negatively related to sea surface temperatures where they foraged. Blood mercury concentrations were also positively related to δ15N. Storm-petrels breeding at Newfoundland colonies consistently foraged over deep ocean beyond the edge of the continental shelf and had higher blood mercury levels. In contrast, some birds in the Gulf of Maine foraged over shallow ocean on the continental shelf and had lower blood mercury concentrations. Determining mercury concentrations in the blood of these seabirds, along with their foraging patterns, allows us learn about methylmercury dynamics in offshore ocean foodwebs.

2h-2: Mercury cycling in response to ecosystem perturbations

FO-017

MERCURY CYCLE IN HYDROELECTRIC BOREAL RESERVOIRS IN QUÉBEC, CANADA

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At the La Grande hydroelectric complex located in northern Qubec, Canada, the evolution of mercury (Hg) was monitored for over 35 years in natural and modified environments. Hg and methylmercury (MeHg) measurements were carried out in soil, sediment and biota (plankton, insects, fish) to better understand the processes involved in the mercury cycle and ultimately, understand and predict the impact of hydroelectric reservoirs. Impoundment of reservoirs leads to the conversion (Hg to MeHg) and circulation of Hg already present in plants and flooded soil in the aquatic environment. This organic form, MeHg, is easily accumulated by living organisms, from plankton and aquatic insects to fish that can be consumed by humans. In reservoirs, concentrations in all fish species increased rapidly after impoundment, peaking after 5 to 13 years in non-piscivorous species, and after 9 to 14 years in piscivorous species. These concentrations increase at levels 2 to 8 times higher than those measured in surrounding natural lakes. Depending on the reservoir, the return to levels found in fish of natural surrounding lakes was completed after 10 to 20 years for non-piscivorous species and after 20 to 31 years in most piscivorous species. Contamination of the food chain is mainly explained by changes in the Hg form present in soil after impoundment. The progressive methylation of initial inorganic Hg content increased from 1% in natural soil and up to 30% after 13 years of flooding. The following mechanisms appear to be most important in the increasing mercury level in fish: 1) increased bacterial methylation of Hg and its passive diffusion through the water column; 2) erosion of flooded organic matter in the drawdown zone, which makes fine, Hg-rich organic particles available for aquatic filter feeders, and active transfer of Hg by aquatic insects burrowing in flooded soil rich in MeHg; 3) periphyton development on flooded soils and vegetation, which promotes the methylation of Hg and its active transfer to fish via aquatic insects and zooplankton feeding on it. The increased MeHg production generally ends 8 to 10 years after impoundment due to rapid depletion of the readily decomposable elements of flooded soil and vegetation. After this time, MeHg transfer to fish by periphyton, zooplankton and insect larvae is reduced to levels occurring in natural lakes.

FO-018

METHYLMERCURY PRODUCTION IN URBAN STORMWATER PONDS

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Stormwater ponds are a type of green infrastructure that effectively manage erosion, flooding, and pollutant loadings related to new residential and industrial development. Stormwater ponds are effective sinks for total mercury (Hg), but very little is known about their capacity to contribute significantly to the production of methylmercury (MeHg). Moreover, the spatial variability in Hg methylation, the possible geochemical and biological controls, and the impact of active management in these systems on MeHg production are entirely unknown. This characterization is necessary to better inform green infrastructure design that reduces MeHg-associated risk; for example, understanding spatial variability is important for inferring implications related to the extent of island and mid-bay bar construction in these systems. Here, we present Hg methylation potential rate constants (K-meth) and sediment MeHg and inorganic Hg concentrations in relation to a suite of ancillary biogeochemical and plant community data from several stormwater ponds across seasons within the Greater Toronto Area in Ontario, Canada. We find significant in situ MeHg production (mean K-meth increases with pond age up to 0.06 / day) in stormwater pond sediment. Mercury methylation rate constants and MeHg concentrations in older stormwater ponds are not substantially different from most other natural and constructed wetlands, whereas MeHg production and concentrations in younger stormwater ponds are lower in comparison. The approximate 10-15 year dredging management cycle of stormwater ponds significantly reduces mercury methylation and MeHg concentrations by removing organic sediment, but only temporarily, as K-meth values and MeHg concentrations increase nearly to pre-dredging levels within a single year. The role of aquatic plants and rhizosphere processes in controlling MeHg production in stormwater ponds is ambiguous; however organic matter availability and links with nitrogen cycling are important modulators of MeHg in these systems. The capacity of stormwater ponds to produce MeHg indicates a need for better characterization of both the MeHg mass balance of these systems and potential biological risk.

FO-019

MERCURY TRANSFORMATIONS IN RESUSPENDED CONTAMINATED SEDIMENTS CONTROLLED BY REDOX CONDITIONS, MERCURY SPECIATION AND SOURCES OF ORGANIC MATTER

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Legacy mercury (Hg) contaminated sediments can be a significant source of Hg to the aquatic system and atmosphere. The release of Hg can potentially be enhanced by various sediment perturbation processes, but the biogeochemical factors controlling Hg dynamics under transient redox resuspension events remain unclear. Solubility and transformation processes of Hg were investigated at different depths (0-2, 0-5 and 0-10 cm) in Hg contaminated pulp fiber sediment microcosms subjected to different levels of oxidation. Four different chemical species of inorganic divalent Hg (HgII) and methyl mercury (MeHg), enriched in different Hg isotope tracers, were added to sediment-bottom water microcosm systems: 201Hg(NO3)2(aq), 202HgII adsorbed to natural organic matter (202HgII-NOM), 198HgII as microcrystalline metacinnabar (β-198HgS(s)) and Me204HgCl(aq). The microcosms were exposed to air for different time periods (0-24h) and thereby spanned a wide range of redox potential, as reflected by a dissolved sulfide concentration range of ≤ 0.3 - 97 μM. The potential methylation rate constant (kmeth) and net formation of ambient MeHg (MeHg/THg molar ratio) were enhanced by up to 50% and a factor of 4, respectively at intermediate oxidation of the sediment microcosms, likely because of an observed 2-fold increase in sulfate concentration stimulating the activity of sulfate reducing bacteria methylating HgII. Differences in the chemical speciation of HgII in the solid/adsorbed phase caused kmeth to vary by a factor of 11-70 in this study due to differences in HgII partitioning for the different species. Chemical speciation was a major controlling factor both for the absolute HgII methylation rate, and for the response in the rate following increased oxidation of the system. The composition of organic matter (OM) varied with sediment depth such that compared to the deeper sediments, the 0-2 cm sediment contained a 2-fold higher proportion of labile OM originating from algal and terrestrial inputs, which serve as metabolic electron donor for microorganisms. This caused kmeth to be up to a factor of 3 higher in the 0-2 cm sediment compared to the deeper ones. The kmeth was lowest and constrained by redox-driven solubility for the β-198HgS(s), intermediate and controlled by both HgII solubility and bacterial activity for the 202HgII-NOM tracer, and highest and controlled by bacterial activity for the 201Hg(NO3)2(aq) tracer. The results in this study provide important knowledge to identify "high-risk" contaminated sites regarding reactivation of Hg following transient redox resuspension events.

FO-020

RESPONSE OF STREAMWATER MERCURY CONCENTRATIONS TO WATERSHED AND IN-STREAM LIME APPLICATIONS IN AN ADIRONDACK, USA WATERSHED

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In the Honnedaga liming project the response of mercury (Hg) and dissolved organic carbon (DOC) are investigated in response to both watershed and in-channel additions of calcium carbonate. In northern Europe and northeastern North America, many aquatic ecosystems are experiencing increases in DOC concentrations as a result of decreases in acidic deposition. These increases in DOC have been correlated with elevated concentrations of Hg in fish. Large scale changes in biogeochemical cycling are being driven by processes such as climate change and recovery from acidic deposition. Honnedaga Lake, located in the southwestern Adirondack Park of New York State has been recovering from acidic deposition. Despite improvements in chemistry, many of the tributaries to Honnedaga Lake remain chronically or episodically acidic, which has limited successful reproduction of lake-resident heritage strain Brook Trout (Salvelinus fontinalis) in these critical spawning and nursery habitats. To improve tributary chemistry and enhance Brook Trout recruitment to the lakes population, lime was applied once in 2013 to the watershed of a chronically-acidic tributary, and every year during 2013-2015 to an episodically acidic tributary stream channel. In this study, we examine the impact of watershed and in-channel liming on streamwater Hg dynamics, including DOC concentrations. The watershed lime application resulted in increases in concentrations of DOC (18.4 mg C/L), total Hg (5.50 ng/L) and methyl Hg (1.94 ng/L) to previously unobserved levels. The MeHg concentrations were not significantly different, even though DOC and THg remained significantly elevated. Stream water of the tributary to which lime was directly applied exhibited a similar response, with short lived increases in Hg following annual applications. The results showed that mobilization of dissolved organic carbon from soils to surface waters may facilitate increases in Hg concentrations because of a strong affinity for Hg. This research suggests that concentrations of THg in streams may increase as impacted systems return to pre-acidification conditions.

FO-021

SPATIAL PATTERNS AND TEMPORAL TRENDS IN ATMOSPHERIC DEPOSITION, SURFACE WATER AND FISH MERCURY IN THE ADIRONDACK REGION OF NEW YORK, USA

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While the Adirondack region of New York experiences modest atmospheric mercury deposition, it is considered a biological mercury hotspot. The Adirondacks are also recovering from severe impacts of acid deposition. Wet and litter mercury deposition, and stream and lake mercury are monitored at Huntington Forest in the central Adirondacks. We have found no changes in wet mercury deposition since measurements were initiated in 2000, but litter mercury appears to be decreasing. Arbutus Lake inlet and outlet samples at Huntington Forest show long-term decreases in concentrations and fluxes of both total and methyl mercury, despite increases in dissolved organic carbon. More broadly we examined spatial patterns and temporal trends in mercury in standard length yellow perch (Perca flavescens) across Adirondack lakes. We find elevated concentrations of mercury in fish, particularly in the western Adirondacks. Mercury in yellow perch are elevated in lakes with low pH and acid neutralizing capacity and high concentrations of monomeric aluminum, indicative of sites acidified by acid deposition. We did not observe any relationship between fish mercury and lake concentrations of dissolved organic carbon, although we did find strong correlations between total and methyl mercury concentrations and dissolved organic carbon in the water column. 17 Adirondack lakes have multiple year observations of mercury in yellow perch. Trend analysis indicates that all but one of these lake are showing statistically significant decreases in mercury concentration at a mean rate of 0.007 μg g-1 ww yr-1, with the greatest decreases occurring in lakes with the lowest pH and acid neutralizing capacity. These patterns suggest strong linkages between effects of acid and mercury deposition, and recovery of fish mercury may reflect emission control of both contaminants.

FO-022

POTENTIAL FOR WATER LEVEL REGULATION IN THE ST. LAWRENCE RIVER TO AFFECT SUSTAINABLE FISH POPULATIONS IN THE FACE OF MERCURY BIOACCUMULATION

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The International Joint Commission is enacting a plan (Plan 2014) to alter water levels above the Moses-Saunders power dam to simulate natural fluctuations and restore biodiversity in this river ecosystem. If the dominant macrophyte, Typha, is reduced in abundance, there is potential for large amounts of sediment, containing mercury (Hg), to become mobilized into the food web. Hg becomes hazardous if sulfate-reducing bacteria (SRB) are present. The St. Lawrence River has historically been impacted by fossil fuel emissions that deposit both sulfur and Hg. Due to extensive Typha, there is likely sufficient organic matter and phosphorous to support SRB. Here, the capacity of upper St. Lawrence River wetlands to support SRB was determined by quantifying concentrations of total mercury, sulfur, phosphorous and organic matter, as well as extracting SRB and Hg-methylating genes from sediments. Four wetland types were compared: barrier beaches, drowned river mouths, protected embayments and open embayments. Protected embayments contained significantly higher Hg concentrations than other wetland types. An estimated 71kgof Hg will be re-suspended and flushed downstream should water levels fluctuate post-enactment of Plan 2014. In addition to economic costs from decreasing water flow through the dam, costs to fish population sustainability from Hg bioaccumulation need be considered. Hg concentrations in water and methylmercury (MeHg) concentrations in wildlife, such as predatory fish and water birds, need to be monitored as Plan 2014 ensues.

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FO-023

HG RETENTION AND TRANSPORT IN TERRESTRIAL ECOSYSTEMS IN THE INTERMOUNTAIN WEST, U.S.A. FOLLOWING SEVERE WILDFIRE

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Vegetation and soil are known reservoirs for atmospheric mercury (Hg) uptake and sequestration. Wildfire is an important ecosystem perturbation, releasing stored Hg back to the atmosphere and also changing important ecosystem properties including canopy cover and soil structure and quality. A limited number of studies have quantified the release of Hg to the atmosphere from wildfire, confirming that there are losses of Hg from vegetation and soil during a fire, with the duration and intensity of heating affecting the amount of Hg loss. Beyond the release of Hg to the atmosphere at the time of the fire, it is also beneficial to understand how Hg is cycled within the ecosystem following a severe fire, specifically the ability of the soil to take up, retain, and transport Hg as the ecosystem recovers from the disturbance. This has implications for Hg transport to aquatic ecosystems as well as the fate of atmospherically deposited Hg. To assess the impact of severe fire on Hg retention and transport within forest ecosystems, we quantified the Hg and carbon (C) content of soil cores collected within the burn scars and nearby reference sites of three severe 2002 wildfires in Colorado, U.S.A. The fires encompass large precipitation and ecosystem gradients (ranging from relatively dry montane Ponderosa forests to relatively wet subalpine Fir-Spruce forests) and there is little forest regrowth more than a decade later. Soil cores were divided into 1-cm increments and separated into coarse and fine fractions. As samples were collected on the toe slope, mid-slope, and crest of the representative watershed in each site, we have a unique opportunity to look at the effects of hillslope mobilization of soil-bound Hg. Analysis of the crest sites shows relatively similar Hg content in the top 6-cm of soil (ranging from 5.27 to 16.4 g Hg/ha, on average) between burned and unburned sites, indicative of relatively low Hg accumulation. We

also find the Hg:C molar ratio in the coarse and fine fractions to be significantly higher at the burned sites compared to their corresponding unburned sites, consistent with Hg uptake from atmospheric deposition in the absence of C input in the burn areas. In addition to the effects of hillslope transport, the low moisture content and relatively organic-poor soil in these Intermountain West ecosystems allow us to isolate the effect of the forest canopy on Hg uptake and retention in comparison to the burn scars with no canopy.

FO-024

MERCURY BINDING BY ASH-LADEN SEDIMENT GENERATED BY WILDFIRE INCREASES FOLLOWING SIMULATED RESERVOIR DEPOSITION

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Erosion of watersheds following wildfire leads to the deposition of ash-laden sediment and associated mercury in receiving water bodies. This study investigated the influence of reducing conditions on total mercury retention and divalent mercury (Hg(II)) binding in ash-laden sediments. Sediments were collected from a watershed that had burned within five months. Sediments were incubated under anoxic conditions to simulate reservoir deposition. Pore water was sampled over 30 days to monitor total mercury, dissolved organic matter, and major ions as the surface sediments transitioned from oxic to sulfate-reducing conditions. The organic matter of the sediments was characterized using sulfur X-ray absorption near-edge structure spectroscopy to assess changes in sulfur oxidation state. A competitive ligand exchange technique was used to quantify changes in Hg(II) binding capacity of the sediment. Over the incubation period, sulfur oxidation state transitions were observed as a loss of highly oxidized sulfur (ΔSox = -9%), and an increase in reduced organic sulfur (ΔSred = +10%). Some of the total mercury in the sediment was initially released to pore water (0.2%), but the transition to reducing conditions produced increased association between total aqueous mercury and the ash-laden sediment. The reducing conditions resulted in a 60% decrease of filter-passing total mercury (≤ 0.2 µm) and an 80% decrease in colloidal total mercury (0.2 µm ≤ X ≤ 10 µm) in the porewater over the 30 day incubation. During the incubation, Hg(II) binding capacity of ash-laden sediment increased by 10-fold based on competitive ligand exchange measurements. The results of this study demonstrate that ash-laden sediments deposited following wildfire can sequester more Hg(II) if the sediment is subjected to reducing conditions following burial.

2i: Regional and local scale stable isotope studies of mercury biogeochemical cycling and bioaccumulation

FO-025

A MERCURY ISOTOPE STUDY ON TERRESTRIAL - ATMOSPHERE MERCURY EXCHANGE IN THE ARCTIC TUNDRA

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Atmospheric Hg deposition to Polar Regions has been extensively studied in coastal zones with the goal to better understand the nature and relevance of AMDE's. Little attention has been given so far to the interior, continental Arctic. We will present a comprehensive Hg stable isotope mass balance of the arctic tundra made at Toolik Field station, AK and compare our findings with extensive terrestrial - atmosphere Hg0 flux measurements conducted at the same site. We measured stable Hg isotope signatures of all important atmospheric (Hg0, HgII in precipitation, HgII from AMDE's) and geogenic (bedrock) sources and major ecosystem reservoirs (vegetation, organic and mineral soils).

The results suggest that vegetation uptake of gaseous elemental mercury from the atmosphere is the dominant deposition pathway to the terrestrial ecosystem, and contributes about 70% to Hg in organic soils. We have observed large mass-independent Hg isotope anomalies in snow during spring, with minimal D199Hg values of -1.4‰, which are in agreement with previously observed Hg isotope signatures during the AMDE season at the Arctic coast. However, the transfer of HgII from AMDE's to the terrestrial ecosystem does not represent a significant source (0-5 %), suggesting that most HgII deposited during AMDE's was re-emitted prior to snow-melt. The Hg isotope signatures in the soils and the atmosphere show no indication for substantial re-emission of gaseous elemental mercury from the soils.

The Hg stable isotope results agree well with micro-metrological flux measurements conducted at the same location. Both independent approaches suggest that vegetation uptake of gaseous elemental Hg represents the dominant Hg flux between the atmosphere and Arctic tundra soils and they thus represent a net sink for atmospheric Hg.

FO-026

SEDIMENT HG HOTSPOTS IN THE HURON-ERIE CORRIDOR OF THE LAURENTIAN GREAT LAKES HAVE CONTRASTING ISOTOPIC SIGNATURES IN CANADIAN VERSUS US WATERS, DEMONSTRATING LIMITED CROSS-CHANNEL TRANSPORT.

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The Huron-Erie Corridor (HEC) within the Great Lakes of North America is a large riverine connecting channel that flows 157 km through the St. Clair River (SCR), Lake St Clair (LSC), and the Detroit River (DR). The HEC is one of the most industrialized and environmentally impacted areas of the Great Lakes, with highly Hg-contaminated sediment located predominantly on the Canadian side of the SCR and on the US side of the DR. The distribution of Hg in sediment of the HEC is generally thought to be a function of localized anthropogenic inputs; however, tracking the transport and fate of contaminated sediments in large riverine ecosystems is challenging. We used stable Hg isotopes to fingerprint and assess the redistribution of sediment Hg hotspots. Sediment samples from the HEC had a large range in Hg concentration (30-6,760 ng/g) and isotopic composition (δ202Hg = -2.60 to -0.35‰, n=43). Mass independent fractionation was typically small (mean Δ199Hg = 0.06 ± 0.05‰, 1SD). Local background sediment (30 ± 1 ng/g Hg, 1SD, n=3) had a mean δ202Hg value of -1.59 ± 0.15‰ (1SD). Mercury-contaminated sediment from Canadian waters of the SCR (2,560-3,100 ng/g) displayed the most negative δ202Hg values (mean δ202Hg: -2.55 ± 0.07‰, 1SD, n=2), resulting from historic chlor-alkali operations. Within the upstream reach of the DR, sediment had moderately elevated Hg concentrations (150-250 ng/g, n=4) and was isotopically similar in Canadian and US waters (δ202Hg values from -2.03 to -1.49‰ and -1.89 to -1.65‰, ± 0.11‰, 2SD; respectively), with the exception of one sample from along the US shoreline (80 ng/g Hg, δ202Hg = -1.19 ± 0.11‰, 2SD), generally suggesting the influence of upstream inputs from SCR and LSC. Within the midstream and downstream DR, in contrast, the isotopic composition of Hg in sediment from US waters (δ202Hg = -1.53 to -0.43 ± 11‰, 2SD, n=15) was distinct from Canadian waters (δ202Hg = -1.94 to -1.60 ± 0.11‰, 2SD, n=11), excluding one outlier. Our results suggest a complex mosaic of localized mercury sources with limited cross-channel transport and demonstrates the utility of Hg isotopes to improve our understanding of contaminated sediment redistribution in large riverine ecosystems. Moreover, the large variation in isotopic composition among high Hg concentration sediment hotspots demonstrates that industrial processes can fractionate Hg prior to release, and that caution should be used when choosing mixing model end members to represent industrial releases on regional scales.

FO-027

MERCURY ISOTOPIC COMPOSITIONS IN WATER COLUMN OF THE HIGH LATITUDE FORESTED LAKES

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Lakes are important ecosystems where mercury (Hg) may be methylated into methylmercury (MMHg) which can pose serious threat on aquatic ecosystem through food web bioaccumulation. Therefore, it's crucial to understand the sources and biogeochemical processes of Hg in lake systems. Recent studies demonstrated that mercury isotope composition is a powerful tool for tracing its behaviors in the environment (1). Nevertheless, limited by pre-treatment method of dilute Hg in natural water, few studies were carried out on Hg isotope compositions in lake systems (2), and weather the Hg isotopic fractionation could be triggered by in-lake processes still remain unclear. The forested lakes characterized by high TOC concentration in high latitude region are such important concern, because the stratification in water column caused by temperature gradient in summer and the decrease of illumination intensity downward (due to the high TOC content) may trigger different Hg isotopic fractionation.

In this study, samples from water columns of seven lakes in Finland and Sweden were collected to investigate the fractionation mechanisms of Hg isotopes. Preliminary results showed that the stratification phenomenon is obvious in these lakes in summer. A concomitant decrease of δ 202Hg and Δ199Hg values towards deeper water was observed, likely caused by the various isotopic fractionations induced by in-lake processes at different layers. In fact, the Δ199Hg/ Δ201Hg ratio in surface water is about 1.03, very close to that found in the photoreduction of Hg2+ (3), indicating that the Hg isotopic signature in surface water is potentially derived from photoreduction of Hg2+, with a possible contribution of rainwater. The Δ199Hg/ Δ201Hg slope in middle water is 1.19, between 1.00 of Hg2+ photoreduction and 1.36 of photo-degradation of MMHg, possibly suggesting a mixture of these two processes. Finally, the Δ199Hg/ Δ201Hg ratio in bottom water is around 1.64, similar to the Δ199Hg/ Δ201Hg (~1.6) introduced by dark reduction of Hg (4), suggesting a possible control of dark reduction. Thus, the application of mercury isotopes may be helpful for better understanding the biogeochemical cycle of Hg in complicated lake systems.

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FO-028

IDENTIFICATION OF TWO ISOTOPICALLY DISTINCT INDUSTRIAL MERCURY END-MEMBERS IN THE SOUTH RIVER, VA

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Historic point source mercury (Hg) inputs from industrial processes on the South River (Waynesboro, Virginia) ended many decades ago, however concentrations of Hg in the physical reservoirs of the South River remain elevated relative to regional background concentrations. To better understand Hg sources, mobility, and bioavailability in the South River, we analyzed THg concentrations and Hg stable isotope compositions of streambed sediments, bank soils, suspended particles, and filtered surface and bank pore waters. An end-member mixing model is proposed which identifies three isotopically distinct pools of Hg in the South River channel environment near the historic point source. In addition to isotopically distinct regional background (low THg conc., δ202Hg≅-1.22‰) and contamination-derived Hg sources (high THg conc., δ202Hg≅-0.59‰), a third end-member was identified with high THg concentrations and relatively low δ202Hg values (δ202Hg≅-1.00‰). To further elucidate the potential source of this previously unidentified Hg end-member and to constrain the end-member isotopic compositions, higher spatial resolution sampling was conducted of previously collected abiotic Hg reservoirs and of channel-margin hyporheic waters near the historic Hg point source. These analyses will better constrain the Hg isotope composition in the river reaches in which the unknown Hg end-member is present and may allow for determination of the processes from which the unknown Hg end-member originates. Additionally, high volume sampling of uncontaminated waters upstream of the former industrial facility was conducted to more accurately determine the Hg isotopic composition of the regional background end-members. Analysis of the Hg isotope composition of dated sediment cores from a Hg contamination impacted floodplain will further constrain the temporal variability of the Hg isotopic composition of legacy Hg released from the former industrial facility. By improving understanding about the spatial and temporal variations in Hg isotopic composition, this study aims to provide insights into the processes that control Hg mobility in the South River.

FO-029

MERCURY SPECIATION AND ISOTOPE SIGNATURES IN SOILS AND GROUNDWATER AT A HGCL₂ CONTAMINATED SITE - EVIDENCE FOR FRACTIONATION PROCESSES DURING SPECIES TRANSFORMATIONS CONTROLLING HG MOBILITY

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Even though Hg has now been phased out in most industrial applications, a large number of legacy sites exist that have been affected by historical Hg releases. Elevated Hg levels in soils and waters at these sites represent a serious threat for the environment at local and regional scales. The long-term fate, mobility, and bioavailability of Hg strongly depend on its speciation, which is determined by the initial Hg compound from the industrial contamination source as well as biogeochemical transformation processes after release into the environment. Understanding the governing processes and controls on Hg speciation in contaminated subsurface environments is essential for risk assessment and site management.

Transformations of Hg species cause mass-dependent and mass-independent fractionation of stable Hg isotopes. Thus, variations in Hg isotope signatures may help identifying and quantifying transformation processes of Hg species. Previous studies at contaminated sites have largely focused on Hg isotopes as source tracer, whereas the application as process tracer has not been sufficiently explored yet.

Here, we present Hg speciation and isotope data from soil and groundwater collected at a former industrial facility in SW-Germany where wood was preserved by $HgCl_2$ treatment (kyanization). Up to 25 tons of $HgCl_2$ have been released to soil and aquifer during operation, resulting in a groundwater contamination plume of 1.3 km length. However, fast flowing groundwater and high Hg concentrations contrast sharply with extremely slow plume movement. It is unclear whether sorption/desorption or species transformation processes control the strong Hg retardation in the subsurface.

Thermodesorption analyses indicated the presence of different Hg species and partial transformation of $HgCl_2$ to Hg^0 in the contaminated soil layers (up to 635 $\mu g\ g^{-1}$ Hg). Isotope analyses by CV-MC-ICP-MS revealed significant d^{202}Hg variations between sections of a soil core taken close to the contamination source and groundwater collected nearby. Most groundwater samples (up to 192 $\mu g\ L^{-1}$ Hg) were enriched in heavy Hg isotopes (up to +0.75‰) relative to NIST-3133. The most contaminated soil layers exhibited d^{202}Hg values of -0.4‰, consistent with signatures of industrial Hg sources, whereas layers with lower Hg contents were isotopically heavier. Sequential extractions revealed significant variations between different Hg soil pools, e.g., isotopically heavy water-extractable Hg relative to bulk soil in the most contaminated layers. Our findings provide evidence for Hg isotope fractionation in the subsurface of contaminated sites and indicate the potential of Hg isotope signatures as tracer for species transformation processes controlling Hg mobility.

FO-030

CHANGES IN STABLE ISOTOPE COMPOSITION IN LAKE MICHIGAN TROUT – A 40 YEAR PERSPECTIVE

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Researchers have frequently sought to use environmental archives of sediment, peat and glacial ice to try and assess historical trends in atmospheric mercury (Hg) deposition to aquatic ecosystems. While this information is valuable in the context of identifying temporal source trends, these types of assessments cannot account for likely changes in bioavailability of Hg sources that are tied to the formation of methylmercury (MeHg) and accumulation in fish tissues. For this study we propose the use of long-term fish archives and Hg stable isotope determination as an improved means to relate temporal changes in fish Hg levels to varying Hg sources in the Great Lakes. For this study we acquired 180 archived fish composites from Lake Michigan over a 40-year time period (1975 to 2014) from the Great Lakes Fish Monitoring and Surveillance Program, which were analyzed for their total Hg content and Hg isotope abundances. The results reveal that Hg sources to Lake Michigan trout (Salvelinus namaycush) have encountered considerable changes as well as a large shift in the food web trophic position as a result of the introduction of several invasive species, especially the recent invasion of dreissenid mussels. Total Hg concentrations span a large range (1,600 to 150 ng g-1) and exhibit large variations from 1975 to 1985. Δ199Hg signatures similarly exhibit large variation (3.2 to 6.9‰) until 1985, followed by less variation through the end of the data record in 2014. δ202Hg showed a relatively consistent value of about 0.4 – 0.8‰ from 1975 to 1988, followed by a significant ($P<0.0001$) shift of about 0.7‰ between 1989 and 1996, with relative stability through the end of the record (1.2 - 1.6‰). This δ202Hg shift may be linked to a combination of the contemporaneous implementation of Clear Air Act rules limiting Hg emissions from waste incineration and to changes in carbon cycling resulting from invasive mussels. Utilizing annual Hg stable isotope variability, we propose a dietary convergence in trout isotope values is observable following the onset of dreissenid invasion. We aim to independently confirm this observation using more traditional stable isotopes (C and N) as well as statistical modeling of isotopic shifts. We propose that with the combined use of Hg, C and N stable isotopes, we can begin to identify how Hg in fish have been affected by shifting sources portfolios of Hg and restructuring of food webs over the past 40 years in Lake Michigan.

FO-031

MERCURY ISOTOPE FRACTIONATION IN THE IDRIJA MINING REGION, SLOVENIA

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Idrija mercury mine is world second largest with 500 years history and total production of 144.800 tons of mercury, which represents over 13% of the entire world production. During that time, 107.700 tons of commercial mercury have been sold and 37.100 tons of mercury were lost into the environment which is after 20 years of mine closure still persistent in local environment. Mercury is present in two main forms as cinnabar ore (70%) and as native Hg(0) (30%). Nowadays, the main sources of Hg in Idrija are: still active mine ventilation shafts, evaporation of Hg from the heavily polluted surroundings of the former smelting plant, mineralized rock dumps of primary or partially exploited ore, outcrops of the ore deposit, and ore residues treated in various ways. Novel methodologies and approaches are developed and used, based on identification of mercury isotope fractionation caused by different processes and sources of Hg during formation of Idrija mine in Triassic. This will enable identification of mercury isotope ratios (IR) characteristic for different environmental Hg sources and reconstruction of Hg mass balance in wider Idrija environment, and will significantly contribute to assess dynamics and transformations of mercury between former mining and smelting operations and local environment. The objective of this research was to study Hg isotopic compositions and evaluate Hg isotopic fractionation of different ores from the mercury mine, processed (retorted) ore, native elemental Hg present in the mine and appeared in near-by Idrijca river, and elemental Hg, produced in Idrija smelting plant. Analysis has been done on Cold Vapour Generator system (CVG) coupled with MC-ICP-MS (Nu plasma II, Nu instruments Ltd, UK). Initial measurements showed huge difference in δ202Hg values were obtained for elemental Hg, from -4.06 ± 0.19 ‰ in produced mercury to -0.74 ± 0.12 ‰ in the native mercury from the mine, whereas the native mercury from the Idrijca river presented δ202Hg value of -0.35 ± 0.15‰. Soil core samples from different locations in the mining district were analysed and δ202Hg values from -1.11 to 0.26 ‰ (2SD = 0.20 ‰) are presented. Hg isotope fingerprints in core samples close to the smelting plant show a big difference in comparison with other cores. The results, which give new information about Hg sources in Idrija mining region, will be presented.

FO-032

CAN GOLD-MINING IMPACTS ON THE AQUATIC FOOD CHAIN OF THE OYAPOCK RIVER BASIN BE DISCRIMINATED BY MERCURY STABLE ISOTOPES?

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French Guiana is subjected to intense gold-mining since 1850. Amalgamation of gold with liquid Hg(0) is the main exploitation process and, once in the environment, Hg is subjected to various biogeochemical transformations leading to its methylation in monomethylmercury (MMHg). This study aims to determine the influence of gold-mining activities on fish Hg contamination. Fish constitutes the main source of proteins of indigenous populations and their high MMHg concentrations could impact human health. We studied total concentration, speciation and stable isotopes fractionation of Hg in fish of both mining (Camopi) and pristine (Trois Sauts) areas along the Oyapock River and tributaries, in French Guiana.

In six fish piscivorous and periphytophageous species studied, a bioaccumulation of Hg along the trophic chain was clearly shown, with average THg concentrations varying from 20 ng.g-1 d.w. in herbivorous species to up to 1750 ng.g-1 d.w. in piscivorous species for the whole Oyapock R. basin. In the mining area, average THg concentrations in piscivorous species (2450 ng.g-1 d.w.) are significantly higher than in the pristine area (1570 ng.g-1 d.w.) while no significant difference is noticed for periphytophageous species. Speciation analysis showed that Hg in flesh was mainly in the organic form even in periphytophageous fish, representing 75% to 90% of the THg. Analyses of N and C stable isotopes also revealed differences between the two locations: two species (one herbivorous and one periphytophageous) presented different trophic level between Camopi and Trois Sauts, d13C being slightly higher in the gold-mining area than in the pristine one. Consequently, diet of low trophic levels fish species seemed different between both locations. Hg sources in fish could be discriminated with Hg isotope signatures only in piscivorous species. Anomalies D199Hg vs D201Hg linear regression showed a slope of 0.89 at Camopi and 1.30 at Trois Sauts meaning that at Camopi, inorganic Hg undergone photoreduction before methylation and ingestion by piscivorous fish. d13C is correlated with D201Hg in piscivorous fish showing that Hg in Camopi river has different sources than in the Oyapock R. upstream. The positive shift observed in D201Hg in piscivorous (+0.12 ‰) fish species between the pristine and the gold mining area suggests another Hg source in the hydrosystem possibly linked to the gold-mining activities. Periphytophageous species have D201Hg and d202Hg higher than the ones of piscivorous species reflecting the difference of Hg sources inside the trophic chain. The Hg speciation and stable isotopes fractionation study in the aquatic food chain in French Guiana is relevant to limit the Hg exposure of native population.

2k: Mercury in the oil and gas industry, from initial exploration through production to end-of-life decommissioning

FO-033

IMPROVED EARLY DETECTION OF MERCURY FOR OIL AND GAS DEVELOPMENTS

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Detection of mercury in early stages of oil and gas project development allows for better incorporation of facility designs and HES procedures to manage potential risks associated with produced fluids. The ability to detect mercury during exploration and appraisal drilling activities has improved through enhancements to mercury analysis of downhole samples, and increased knowledge of the key geologic risk factors. This presentation will discuss an improvement to the analysis of downhole fluid samples for mercury content, and illustrate various limitations with conventional analysis methods. The improved analysis method includes a post-wash of samples chambers to capture mercury which is retained in sample chambers (even with so-called inert coatings) this retention can range from minimal to concentrations exceeding 1 ppm wt. of the original reservoir fluid. Under some circumstances, conventional analysis of downhole samples can significantly under report mercury concentrations. The importance of rigorous QA/QC protocols will be highlighted. Reservoir mercury results will be shared that indicate that bottom-hole temperature might correlate with mercury concentration in produced fluids, and that the equilibrium of mercury and mercury sulfide in the reservoir could be the basis for this correlation.

FO-034

ANALYTICAL CHALLENGES - DETERMINATION OF MERCURY IN RAW WET NATURAL GAS

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The determination of Hg in natural gas is a well-established procedure which is routinely used by many laboratories at gas processing plants worldwide. ISO 6978 and ASTM 6350 are the two methods that are most commonly used and these methods are based on gold amalgamation with atomic absorption/fluorescence spectrometry. These methods however were developed and originally validated for dry export gas. In this case, the sample matrix is relatively simple as the sample has undergone numerous gas processing purification steps including dehydration, acid gas treatment, removal of contaminants such as hydrogen sulphide and mercury and also separation of heavier hydrocarbons. When the methods are applied to sample point locations upstream of gas treatment numerous issues may be encountered and as such special sampling precautions have to be made to ensure that the accuracy of the method is not compromised. Data will be presented from an inter-laboratory field study highlighting the complications of determining Hg in raw untreated natural gas.

Laboratory studies were subsequently conducted using a simulated raw natural gas stream containing saturated water and BTEX components. The gas stream was spiked with a known concentration of elemental Hg using a dynamic Hg generator system. The effect of these components on the accuracy of gold amalgamation with atomic fluorescence was studied. Several types of gold adsorbents including silica coated with gold nanoparticles and gold-platinum wire were studied at different collection temperatures. This work led to the development of a new sampling arrangement which was tested in the field on wet untreated natural gas. Field data will be presented from gas plant in Egypt where upstream measurements of Hg are conducted as process monitoring on site. This accuracy of the measurement is crucially important to the oil gas and petrochemical industry because of the requirements of these sites to fully understand the fate and transport of Hg across the processing plant.

FO-035

DEMERCURISATION SOLUTION TO PURIFY STREAMS CONTAINING MERCURY UNDER DIFFERENT FORMS

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Elemental mercury is a natural contaminant of hydrocarbons streams (natural gas, gas condensates, crude oil). In particular, mercury is a safety issue in LNG plants, as mercury forms amalgams with aluminum-based alloys, leading to corrosion issues on cryogenic exchangers required to liquefy natural gas. In hydrocarbon cuts, it will poison refining catalysts, especially those containing noble metals.

In natural gas, mercury is essentially present as elemental mercury. However, in crude oil or even in gas condensates, mercury is not necessarily only under this form, especially if they are submitted to air. Indeed, it could be in combination with sulfur. For instance, some streams contain solid particles that have been identified as being HgS. In other case, they are some mercury compounds that cannot be stripped out by gaseous streams. They are considered as refractory compounds. Although their nature are not very well known, it is supposed that at least one part of them are mercury mercaptide, that is to say the result of the reaction between mercury and mercaptans.

Yet, solutions to eliminate elemental mercury are based on redox reaction between elemental mercury and sulfur or metallic sulfur. But if mercury is already at a +II oxidation state as it is the case in HgS or mercury mercaptides, these reactions cannot occur anymore. Consequently either a specific solution has to be developed to trap these others types of mercury compounds, or they have to be transform into elemental mercury before being trapped. This second option is the preferred one as mercury can be under many forms having different reactivity.

The way IFPEN has optimized solutions dedicated to the total elimination of mercury whatever its form is based on the comparison of the behavior of synthetic and real crude oil. The objective was double : verifying that our hypotheses on the nature of refractory mercury compound was reasonable and developing an efficient method to eliminate mercury from all kind of hydrocarbon streams. This implies to decompose mercury compounds and to trap elemental mercury.

FO-036

FUNCTIONAL SPECIATION OF NON-VOLATILE, SOLUBLE FORMS OF MERCURY IN LIQUID HYDROCARBONS (CRUDE OIL, CONDENSATE, NAPHTHA)

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Mercury is a naturally occuring contaminant found in almost all oil and gas reservoirs, existing in a range of concentrations and in a number of different forms.

This causes a number of issues when the oil is processed, including corrosion and the potential for worker exposure and release to the environment. There are a number of options for removal of mercury from liquid hydrocarbons, which are predominantly focused on removal of elemental mercury. In order to understand how much mercury will be removed by a given process the mercury needs to be speciated to ascertain which forms are present. Due to the losses of mercury observed over time when samples are stored and the proven transformation of mercury from one species to another in relatively short time periods in liquid hydrocarbons, it is desirable to perform speciation analysis immediately after sampling. This limits the use of analytical molecular speciation techniques such as GC-ICP-MS since these instrumental techniques are not portable.

The international standard test method UOP-938 allows on-site functional speciation using the physical and chemical properties of mercury species to categorise mercury as; Elemental / soluble ionic / soluble non-ionic / insoluble.

This presentation details work carried out to better understand which mercury compounds are included in the groups labelled soluble ionic and soluble non-ionic as there is very little literature information available on this subject. This study has provided information on which compounds fall into which category, which is valuable in the evaluation of whether a removal technology will in fact remove the mercury (without having to instigate a live trial), and where the mercury can be expected to partition within the hydrocarbon processing system.

FO-037

MANAGING MERCURY CONTAMINATED WASTES FROM THE OIL AND GAS INDUSTRY

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Trace concentrations of mercury are found in all hydrocarbon reservoirs across the world presenting risks to personnel, process equipment, and the environment. The effects of mercury on personnel has been well researched with exposure limits in place for both inhalation and skin absorption exposure routes. The effect of mercury in oil and gas processing equipment has also been well documented due to a number catastrophic, mercury related incidents such as Skikida (Algeria) and Moomba (Australia). In both of these incidents the occurrence of Liquid Metal Embrittlement resulted in critical failure of an aluminum component within the process system. These failures led to explosions, which caused significant damage to the facilities and in the case of Skikida a significant loss of life. Learnings from these incidents have resulted in improved understanding and accepted industry standards for the removal of mercury from feed streams in both oil and gas processing facilities. To date, however no such standards have been developed for the disposal of mercury or mercury associated waste streams that are generated through scrubbing or maintenance activities at these facilities. Waste streams can include mercury contaminated PPE, piping/plant, equipment, sludges, scale and mercury guard bed adsorbents. Treatment processes for mercury waste streams are varied and requirements for disposal are largely driven by regulation. This has resulted in variation of mercury waste management practices not only between geographical regions, but also from country to country.

This session investigates mercury processing technologies and how the limited availability of dedicated mercury treatment facilities has limited standardization of mercury waste management across the industry. It also explores the suitability of the current hub and spoke model utilized by the major mercury recyclers given the requirementsfor international trans-country movements of mercury waste under the Basel Convention.

FO-038

EXPERIMENTAL RESULTS AND PHENOMENOLOGICAL MODELING OF ELEMENTAL MERCURY ADSORPTION ON SULFIDED HYDROXYAPATITE ADSORBENTS

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Hydroxyapatite-based adsorbents have been pointed out as high capacity adsorbents for the mercury removal from liquid or vapor phase. In this work, hydroxyapatites modified with metal sulfides were successfully employed for adsorption of trace elemental mercury (Hg0) from gaseous hydrocarbon streams such as natural gas.

Dynamics of mercury adsorption by the synthesized adsorbents was investigated in a fixed-bed adsorption process, one of most promising technologies for elemental mercury (Hg0) removal from gaseous streams. Four different adsorption tests were carried out with the following operational conditions, respectively for the T-1, T-2, T-3, and T-4 tests: initial mercury concentrations of 9.46, 8.96, 12.5, and 11.2 ng.mL-1; adsorbent metal content of 2.1, 2.1, 5.4 and 4.8 %; bed length of 1.25, 0.5, 0.5, and 1.0 cm. Other conditions are the same for all tests: temperature and diameter of reactor of 301K and 0.5 cm, respectively, and gas flow rate of 30mL.min-1.

A mathematical model were developed based on experimental information of nitrogen physisorption at 77K, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) techniques of the raw and modified adsorbent and thermal desorption of used adsorbent samples. The proposed model includes intraparticle diffusion and chemical reaction between Hg0 and two types of metal sulfides present in the internal surface of adsorbent particle.

Model parameters such as bed porosity, particle porosity and intraparticle diffusion coefficient were calculated based on adsorbent characterization results. Kinetic and maximum capacity parameters were estimated from the experimental breakthrough curves of the two longer adsorption tests (T-1 and T-3, with time duration of 95 and 49 days, respectively). Calculated results were in good agreement with experimental breakthrough curves and estimated model parameters were statistically significant. Indeed, these parameters were validated with the experimental breakthrough curves of the two other adsorption tests (T-2 and T-4) and the similarity between experimental and calculated results corroborate the proposed phenomenology of mercury removal by hydroxyapatite-based adsorbents.

FO-039

THE MITIGATION AND ELIMINATION OF MERCURY BY DECONTAMINATION AND REHABILITATION OF CONTAMINATED PROCESS SYSTEMS, ASSETS AND THEIR WASTE STREAMS FOR SAFER TRANSPORTATION, TREATMENT AND DISPOSAL

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Even though it is just a metal, in industries where Mercury is a naturally occurring contaminant or even a required process component its dynamic and phenomenal cyclic characteristics are still not widely known or fully understood.

Global industry continues to drive forward with production, research, development, adaptation, mitigation, treatment and disposal of mercury, mercury compounds and mercury-contaminated products, but there are still large areas of the industrial process that have yet to be fully or properly addressed, although it could be argued that is mainly due to it being directly related to end-of-life on the process and containment infrastructure. The issue is carbon steel.

Carbon steel acts as a scavenger, capturing any mercury or mercury compounds from within process streams and retaining it, in various conditional states, along the surface of the steel, within layers of corrosion, areas of deposition and within the surface matrix of the steel substrate.

In particular, Mercury contamination can cause problems to offshore processing platforms and other downstream hydrocarbon production facilities, as well as the intermediate infrastructure. The Oil Gas industry is aware of the cycle phenomenon whereby Mercury is absorbed into the surface matrix of carbon steel pipelines during the process and transportation of contaminated hydrocarbon mediums and its subsequent ability to desorb back out from the steel surface and return to those same, or new uncontaminated, streams. However, the fate of the carbon steel pipelines, vessels and equipment falls under further limitations with lengthy, costly and typically unverifiable results until now!

As a growing concern among operators and companies around the world the decommissioning, disassembly and disposal of contaminated assets, subsea pipelines, platforms and refineries has always had its limits with current legislation, and most commercial applications, only dealing with the decontamination of free (adsorbed) Mercury from system internals prior to its decommissioning.

It is now possible to fully remove mercury from the surface matrix of carbon steel, in a repeatable manner, which ensures that the decontaminated carbon steel sections meet the strict acceptance criteria for recycling purposes using a licensed steel smelter.

Understanding the contaminant and how it behaves under certain conditions has been key to developing a selection of decontamination methods and applications that can now be applied quickly and methodically in remote locations as well as sensitive and dynamic environments while also providing flexibility and certainty to meet limited, but licensed, final waste disposal routes and best practices.

FO-040

AXENS MERCURY REMOVAL SOLUTIONS APPROACH FOR OIL & GAS INDUSTRY

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Mercury has to be removed from hydrocarbon streams due to safety issues and to protect health, environment and equipment. We are going to focus on a non-regenerative adsorbent based on the chemical reaction between mercury and the sulphur of active phase (metal sulphide) to form non-hazardous and very stable cinnabar (HgS). The limitation factor of this chemisorption mechanism is the mercury diffusion. Mercury diffusion issues lead to an increase of the axial dispersion inside the vessel which can be responsible for a premature mercury breakthrough. Therefore adsorbents have to be designed to minimize the diffusion issues.

This innovative technology consists of an active phase highly dispersed on an optimized alumina carrier. The specificity of these adsorbents is to maximize the number of active sites accessible for the chemical reaction with the mercury. Indeed, the active sites number has been maximized and the porosity design has been tailored. This alumina carrier is highly mechanically resistant and thanks to its way of preparation, the active phase is strongly linked to the alumina carrier. Different adsorbents devoted to specific gas or liquid application have been developed.

Experience in the manufacturing of mercury removal adsorbents is completed with licensing and associated technical services activities, leading to a mercury removal global offer from design to disposal. This complete integrated offer covers: mercury analyses, pilot tests, on-site tests, process selection, performances and lifetime projections, process design package delivery, skid-mounted packages delivery, adsorbent loading supervision, unit follow-up and adsorbent unloading supervision and spent adsorbent disposal logistic.

Feasibility study of the adsorbent solution and performances simulation are also required for selection of the most appropriate adsorbent for specific operating conditions. The modeling tool takes into account diffusion limitation and provides mercury adsorption profile within adsorbent bed and mercury breakthrough curves versus time. This model fits with pilot tests and industrial units results. On-site tests are also very useful to confirm this selection.

In this presentation the mercury removal performances of the latest adsorbent developed with this technology, AxTrap 283, will be discussed. Then, based on case studies, the interest of the modeling tool and of on-site tests to predict the mercury adsorption profile within adsorbent bed will be highlighted.

4d-4: Technologies and approaches for mitigating mercury emissions

FO-041

CURRENT STATUS OF COMPLIANCE MERCURY MONITORING AT COAL FIRED POWER AND CEMENT PLANTS IN THE USA

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Mercury emissions from coal - fired power and Cement producing plants have been recently regulated in the U.S. by a set of rules set forth in the Mercury and Air Toxics Standards (MATS) and National Emission Standards for Hazardous Air Pollutant (NESHAP). These rules are anticipated to significantly reduce mercury emissions and consequently lower the concentration of mercury in the flue gas effluent from these facilities.

This presentation will give an overview and discuss the current status of mercury measurements and compliance methods available for Plant Operators.

Accumulated field experience on continuous monitoring at very low levels using sorbent trap technology will be presented. As sorbent traps pre-concentrate the sample prior to analysis, they have the ability to accurately measure very low mercury levels. In fact, sorbent trap-based mercury monitors (STMM) might be the only approach that can accurately measure at the levels mandated by MATS.

A number of STMM systems have been operating in states that required mercury emission monitoring prior to MATS. As a result, electric utilities have become familiar with the technology and maintenance requirements and costs are well characterized. Although operating costs are comparable to those of a traditional continuous emission monitoring system (CEMS), the annualized total cost for STMM systems is considerably less.

The disadvantage of sorbent - trap based mercury monitoring is the lack of temporal resolution in the data as would be required for process control. However, STMM systems could be coupled with a CEMS if feedback for process control is needed. The CEMS could be configured just for process intelligence without the constraints when accumulating data for compliance demonstration. Experience from different Power Plants using portable CEMS for process control along with STMM will be presented.

FO-042

IMPROVING MERCURY REMOVAL EFFICIENCY BY CATALYTIC MEANS FOR BITUMINOUS AND LIGNITE FIRED POWER PLANTS IN EUROPE AND NORTH AMERICA

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Mercury emissions from coal - fired power and Cement producing plants have been recently regulated in the U.S. by a set of rules set forth in the Mercury and Air Toxics Standards (MATS) and National Emission Standards for Hazardous Air Pollutant (NESHAP). These rules are anticipated to significantly reduce mercury emissions and consequently lower the concentration of mercury in the flue gas effluent from these facilities.

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FO-043

THERMAL DESORPTION OF HG COMPOUNDS FROM THE WFGD GYPSUM STUDIED BY MASS SPECTROMETRIC DETECTION

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Gypsum is a byproduct of the wet flue gas desulphurization (WFGD) system, which is most commonly used clean technology in the coal burning industry. In addition to gypsum, being the main product of desulphurization process, several other compounds are formed, among which ferro-ferry oxy-hydroxides are very important due to their abundances in WFGD gypsum and their adsorptive properties. The thermal stability of mercury compounds in gypsum has become an important issue recently, due to a potential use of gypsum in the context of circular economy.

In this work, quadrupole mass spectrometer (QMS), with direct sampling into the closed ion source with cross beam configuration was applied as a detector, instead of commonly used CV-AAS. The arrangement enabled us to measure samples with Hg concentration bellow 50 ng g-1 using at least 5 mg of sample. The QMS allows the detection of several ions simultaneously with a dynamic range of 107. In addition to Hg, other ionic species such as HCl+, H2S+, SO2+, SO3+ can also be measured. Unfortunately no correlation could be found with Hg+ ions in desorption spectra, probably due to high difference in Hg+ versus HCl+ etc. concentrations.

Three different gypsum slurries of block 6 were taken from lignite burning power plant. All gypsum slurries were additionally separated into two phases by gravitation (particle size of finer ~0.1-50 µm and coarse ~10-150 µm fraction). Thermograms (desorption spectra) obtained from all analysed samples exhibit one single desorption peak at about 230±20°C. Considering iron as a crucial factor in understanding adsorption/desorption process we performed a number of simulation experiments with and without iron, in the form of FeOOH, using saturated solution of CaSO4·2H2O (~2g/l) and different Hg-compounds such as HgCl2, Hg2Cl2, HgO, HgSO4 and Hg2SO4. In all cases the resulting thermograms (that contain FeOOH) exhibit single peak at similar temperature (230±30°C) irrespective to the form of Hg that was added to gypsum solution showing similar picture to the WFGD samples.

Thermograms obtained in this study differ from those in previous work, where gypsum slurry was taken from different blocks. This reflects importance of WFGD chemistry and APCDs (only block 6 has installed SCR). It is assumed that in a specific gypsum slurry adsorption/binding process of Hg is similar in all cases no matter to Hg-species present. Further studies are needed to confirm this.

FO-044

DFT AND EXPERIMENTAL STUDIES ON EFFECT MECHANISM OF H2S ON MERCURY REMOVAL DURING COAL GASIFICATION

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The development of effective sorbents for Hg0 removal during coal gasification has attracted increasing concern in recent years. H2S presents in the flue gas of coal gasification and plays an important role in Hg0 adsorption. However, the effect of H2S on Hg0 adsorption and the stable forms of mercury on carbon surface during coal gasification are still unclear. Furthermore, there is even controversy on the effect of H2S on Hg0 adsorption. Understanding the effect mechanism of H2S on Hg0 adsorption is important to the design of carbons with faster kinetics and greater capacities for Hg0 removal during coal gasification. The present study addressed the effect mechanism of H2S on Hg0 adsorption at the molecular level by performing density functional calculations. The theoretical results indicate that the Eley-Rideal mechanism with Hg0 adsorption on sulfur adsorbed carbon surface is the most possible reaction process for the formation of HgS. The theoretical results are further verified by experiment and a group of adsorption experiments are conducted. The Hg0 removal efficiency of carbon increases significantly in the presence of H2S. The Hg0 removal efficiency of H2S pre-adsorbed carbon is higher than that of the adsorption on original carbon. This suggests that H2S adsorption can form active sites on carbon surface and then improve the removal of Hg0, which is in good agreement with the DFT calculation results. Temperature programmed desorption results indicate that Hg0 is more likely to be adsorbed by active sites which formed by H2S adsorption. XPS analysis suggests that Hg0 can react with sulfur species on carbon surface. Combining experimental and computational results together, the EleyRideal mechanism with H2S pre-adsorption can be determined.

FO-045

MERCURY ADSORPTION ON POROUS CARBON AND THE EFFECT MECHANISM OF OXYGEN FUNCTIONAL GROUPS

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Porous carbons have ordered pore structure and high surface area, and are much more renewable than activated carbons. They have the potential to remove Hg^0 from flue gas effectively. The Hg^0 removal ability of porous carbon is higher than that of activated carbon. This is owing to the excellent surface physical properties of porous carbon. Non-thermal plasma is used to modify porous carbon to achieve better Hg^0 adsorption efficiency. This modification method can produce active species to improve the surface chemical properties of porous carbon in a less costly way. The results indicate that porous carbon treated with non-thermal plasma has higher Hg^0 removal efficiency than others, and longer treatment time results in higher efficiency. The main reason is that non-thermal plasma treatment increases oxygen functional groups on porous carbon surface, which plays an important role in Hg^0 absorption. Density functional calculations were performed to provide molecular-level understanding of the effects of oxygen functional groups on Hg^0 adsorption on porous carbon. The results indicate that oxygen functional groups can improve the adsorption of Hg^0 because they increase the neighboring site's activity for Hg^0 adsorption.

FO-046

AN EFFICIENT SORBENT BASED ON CUCL2 LOADED CEO2-ZRO2 SOLID SOLUTION FOR ELEMENTAL MERCURY REMOVAL FROM CHLORINE-FREE FLUE GAS

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To remove elemental mercury (Hg0) in chlorine-free coal combustion flue gas efficiently, a series of sorbents based on CuCl2 loaded Ce0.67Zr0.33O2 solid solution (denoted as CuCl2/CZ) were developed. In this way, the abundant Cl and affluent active chemical adsorbed oxygen (O*) on the sorbent would be combined and made full use for Hg0 removal. The XRD, XPS, FSEM-EDX, Raman, TG, and N2 adsorption/desorption were employed to characterize the catalysts. The Hg0 removal behaviors over CuCl2/CZ were studied using a laboratory-scale fixed-bed reactor. The catalyst with optimal loading 6% CuCl2 exhibited better performances (89.6%-97.1%) within a much wider applicable temperature range (100-300°C) in the absence of HCl with a much higher gas hourly space velocity (380,000 h-1). The results indicated that the mercury removal efficiency over CuCl2/CZ was higher than those over the reported CuCl2 supported on Al2O3, Fe2O3, TiO2, activated carbon, zeolites, etc. The interaction between Cl and chemical adsorbed oxygen was probably responsible for its superior performance. The XPS results of the fresh, thermally treated, and spent 6% CuCl2/CZ might explain the Hg0 oxidation process. Hg0 was firstly oxidized by consuming lattice Cl in CuCl2, and reducing it to CuCl. Then, the CuCl will be oxidized to an intermediate product (Cu2OCl2) by O2. As no Cu+ was observed and oxygen enrichment was detected on the spent CuCl2/CZ sorbent, the Cu2OCl2 then could be decomposed and generated CuCl2. In this way, some lattice Cl was consumed and there was no more Cl species in the chlorine-free flue gas which could replenish the consumed lattice Cl. Fortunately, for the 6% CuCl2/CZ, the Hg0 removal efficiency still kept higher than 80% after 24 hour tests with 380,000 h-1 space velocity. The spent catalyst could be regenerated under HCl and O2 stream after thermally treated at 350-450°C. SO2 (1000 ppmv) just slightly inhibited the Hg0 removal efficiency even though there was some steam (5% v/v) in the flue gas.

FO-047

MERCURY BEHAVIOR IN HYBRID FILTER WITH ACTIVATED CARBON COATING

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Air pollutant control devices in coal-fired power plant were mainly consisted of a selective catalyst reactor (SCR), an electrostatic precipitator (ESP) and a flue gas desulfurization (FGD). In this configuration, elemental mercury was oxidized by temperature decrease, existence of complexity, and reaction with halogens. Then the oxidized mercury was usually removed by adsorption in fly ash or wet type control device. As a result, the elemental mercury was dominant in flue gas from coal-fired power plant. Adsorption by activated carbon was introduced as one of the best available technologies in removal of element mercury in flue gas. In this study, mercury removal efficiency was investigated for the Hybrid filter (HF) with activated carbon coating. HF was combined with bag filter and ESP in a single chamber and originally designed to remove fine particulates and retrofitted to the flue gas control device for mercury simultaneously. In lab-scale experiment, pressure drop and mercury removal efficiency were analyzed for determining optimal activated carbon coating rate at the operating facility conditions at a coal-fired power plant. After then, the activated carbon optimally coated filter was applied to the pilot-scale HF which was installed between ESP and FGD in a commercial coal-fired power plant. The effect of activated carbon filter in HF on mercury removal efficiency was investigated by measuring and comparing mercury concentrations between inlet and outlet of HF.

FO-048

MERCURY METHYLATION POTENTIAL OF WASTE CARBON SORBENTS USED FOR MERCURY VAPOR CAPTURE

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Black carbon sorbents, such as activated carbon and biochar, are used for mercury vapor capture for flue gas treatment and other applications. In our previous research, we developed easy-to-manufacture sulfurized activated carbon and biochar sorbents for Hg(0) vapor capture for low-resource end-users such as artisanal mining operations. These sulfurized carbons sorbents substantially reduced Hg vapors in gas streams relative to unsulfurized sorbents. However, the stability and bioavailability of the sorbed Hg, particularly in landfills and other waste disposal impoundments, has not been closely studied. In this research, we examine methylmercury (MeHg) production potential of spent carbon sorbents after incubating in sediment slurries. Five types of carbon sorbents (including sulfurized and unsulfurized activated carbon, biochar, and a commercially produced activated carbon for flue gas application) were each loaded with approximately 10 mg/kg of elemental Hg. The sorbents were added to anaerobic sediment slurries to a mass content of 5% relative to sediment dry mass. A replicate slurry received dissolved Hg as a control to simulate atmospheric deposition or highly reactive Hg. After a 5 day incubation at room temperature, net MeHg production was ten times greater in slurries amended with low-technology sulfurized sorbents as compared to unsulfurized activated carbon or biochar alone. Sulfurized sorbents leached significantly more Hg and sulfate than their non-sulfurized counterparts in desorption experiments performed in parallel to the sediment slurry experiments. Analysis of the sulfurized sorbents via X-ray spectroscopic methods revealed that the sorbents contained a mixture of sulfur species, including sulfate, thiosulfate and reduced sulfur (oxidation state equal to 0 or less). Sorbed Hg tended to co-locate with reduced sulfur on the surface of the carbon particles. The substantial presence of sulfate on the sulfurized sorbents likely contributed to Hg methylation by stimulating the growth of methylating sulfate reducing bacteria in the slurries. This research shows that spent sorbents for Hg vapor capture can have unintended consequences if they are inappropriately disposed.

1g: Mercury through time – Reconstructing Hg-deposition using natural archives

MP-001

SHIFTS IN HISTORIC MERCURY SOURCES IN SELECT UPPER MIDWEST USA LAKES: EVIDENCE FROM MERCURY STABLE ISOTOPES

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Mercury (Hg), a globally distributed air pollutant, primarily enters aquatic ecosystems through watershed runoff, industrial discharges, soil erosion, and direct atmospheric deposition. The distribution of Hg in sediment profiles, coupled with high-resolution age dating (e.g., 210Pb and 137Cs), have been broadly used to evaluate historical changes in Hg inputs. In sediment cores lacking direct contaminant discharges, enrichment factors are typically 2-4 times due to atmospheric inputs. However, in lakes with obvious local contamination histories, it is often difficult to separate atmospheric inputs versus direct point source contamination and other enriched watershed inputs. Recently, stable isotopic Hg analyses of sediment cores have been shown to be powerful tools for identifying specific Hg contamination events in rivers, lakes, and coastal regions. In this study, we investigated the deposition influx and isotopic composition of Hg in several sediment cores from lakes with a history of contamination in the Upper Midwest USA, including Lake Pepin on the Mississippi River, Lake Mendota, and Lake Michigan (open lake and within Green Bay). Mercury influx in these lake cores begin to increase in the mid-1800s, and peaked in the 1970s. In all instances, permanent enrichment of δ202Hg was observed following the onset of industrial contamination. The utility of mass independent fractionation (mainly reported as Δ199Hg) as a tracer for sources and processes became less apparent following industrial contamination. Both Lake Pepin and Lake Michigan exhibit decreases in concentration following the 1970s peak, without obvious changes in isotopic composition, suggestive of a decrease in Hg influx without changes in Hg sources. In order to identify isotopic signatures representative of single sources of Hg in the region, our ongoing studies include sediment cores from lakes with contrasting watershed to lake surface area ratios to assess atmospheric versus watershed influences. Through the comparison of lakes without a history of point source contamination, we expect to develop source attribution models for which we can apply to more complex systems in the Upper Midwest (e.g., Lake Pepin, Lake Mendota and Lake Michigan).

MP-002

EXAMINING THE EFFECTS OF CLEAR-CUT LOGGING-RELATED CANOPY REMOVAL ON HG ACCUMULATION AND STORAGE IN PACIFIC NORTHWEST (USA) OLD-GROWTH FOREST ECOSYSTEMS

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Mercury inputs to forest ecosystems are driven by atmospheric deposition to the forest canopy and soils, and perturbations related to clear-cut logging practices, specifically the removal of the canopy, impact Hg inputs and storage in these terrestrial ecosystems. At our study sites in the tephra fall zone of the 1980 Mt. St Helens volcanic eruption, the tephra deposits provide a clear marker that permits the study of mercury (and carbon) in surficial soils that have developed following the eruption at old-growth forest sites and adjacent sites that were clear-cut just prior to 1980. The ~15cm tephra deposition at these sites crushed the understory and left the forest overstory intact at the old-growth sites, allowing mercury deposition associated with canopy processes and litter deposition to be incorporated into overlying soils. We collected surficial soils and underlying 1980 tephra, at sites with known tree canopy species at the old growth and formerly clear-cut sites to quantify post-1980 mercury accumulation and storage in soils. At the old-growth sites, we mapped tree species and were able to investigate potential differences in the roles that specific species may play in influencing soil mercury accumulation. Overall Hg storage through the tephra layer in the soil at our sites averaged 18.60 ± 6.85 g Hg/ha at old growth and 8.86 ± 4.69 g Hg/ha at clear-cut sites. The organic horizon of the soil accounted for 42% and 16% of Hg storage in the old growth and clear-cut sites respectively. The enhanced Hg storage observed in the old-growth forest soils illustrates the significant role the canopy played in both scavenging Hg from the atmosphere (over the 33 years between sampling and eruption) and likewise in the enhanced Hg retention in underlying soils via carbon addition. A stronger positive correlation between Hg and C concentrations was observed in the old growth sites ($r2 = 0.63$) than in those clear-cut in the past ($r2= 0.49$). We estimate that annual Hg accumulation in soils at old growth and clear-cut sites were 0.51 g Hg/ha/yr and 0.22 g Hg/ha/yr respectively, such that the old growth canopy resulted in 0.29 g Hg/ha/yr more Hg stored in underlying soils.

MP-003

DISTRIBUTION OF TOTAL-HG IN A MARINE SAPROPEL FROM MANGROVE LAKE, BERMUDA

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Mercury (Hg) is a toxic global pollutant emitted by both natural and anthropogenic sources and dispersed through the air. Mercury deposition rates have increased in the past century as documented by lake sediment cores and other markers. Sapropels are organic-rich sediments composed primarily of dead algae, and include forms of sulfur that bind and retain Hg. Investigations into the distribution of Hg in sapropel cores are relatively few and none have been measured on Bermuda, a remote island in the Atlantic Ocean over a 1000 km from the US Coast. Here, we determined total-Hg in two sapropel cores from Mangrove Lake, Bermuda. The cores dated back ~1800 years before present (BP) based on an independent Bayesian-based age depth model. There was a sharp rise in the uppermost layers of the core starting at ~45 cm corresponding to the ~1900's (AD). Mean concentrations in this upper region were 317 ng/g with a high of 420 ng/g (dw basis). There was also a general rise starting around the 1700's with an anomalously high point at ~1800 AD, coinciding with ship and fortress building on the Island. Background (pre-industrialization) levels were generally less than 100 ng/g. However, the lower portion of the two cores differed, with ML3 having a relatively low & consistent background. In contrast, ML1 had added features. From the core bottom, Hg: (1) decreased during ~500 to ~1500 AD, (2) increased from ~1500 to ~1800 AD, (3) spiked at ~1800; (4) leveled out at ~70 ng/g during the 1800's; and (5) rose sharply after. These trends are not fully explained by variations in organic matter. However, the proportion of source water (runoff vs. seawater intrusion) may have changed over time. Bermuda is often impacted hurricanes which have altered deposits to Mangrove Lake. To help interpret Hg profiles, we determined trace elements and isotope ratios using ICPMS. Heavy metals, including Pb, Cr, Cu, Ni and Zn, were elevated in the upper core. Several, but not all, elements followed the same depth profile as Hg, including a spike at ~100-cm (~1800 AD). Isotope ratios indicate gasoline as the likely source of Pb in the upper-most layers. Differences in the lower portion of the two cores is still under scrutiny, however, changes in the lower core demonstrate that early natural fluctuations in Hg must be considered.

MP-004

USING TREE-RINGS TO RECONSTRUCT MERCURY EMISSIONS ASSOCIATED WITH GOLD MINING IN THE KLONDIKE (YUKON TERRITORY)

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Atmospherically mobile Hg(0) can be converted, post-deposition, to toxic methylmercury in terrestrial and aquatic environments posing significant risks to human and ecosystem health in regions far from emission sources. Accurate projections of future Hg exposure and impacts will partly depend on our ability to understand changes in the atmospheric Hg pool, but long-term knowledge of atmospheric Hg variability is limited to ~2 decades of instrumental monitoring. Natural Hg archives such as ice cores, tree-rings and lake sediments have the potential to fill this knowledge gap. Tree-rings are ideal since they are annually resolved, span multiple centuries, and cover large areas of Earth's surface. Few studies concerning a small number of species have shown the potential of tree-rings to record local Hg emissions, but additional proof-of-concept is needed. We present an annually resolved tree-ring Hg record from a stand of white spruce ~100 m from the Bear Creek Gold Room site, Klondike Goldfields, where the Au-Hg amalgam method was used to recover fine gold from placer ore. Bear Creek operations began in 1905, but were greatly expanded in 1930 when most Klondike recovery operations were consolidated to the Bear Creek site. Results from 15 trees reveal a common pattern in tree-ring Hg over the last ~150 years (mean $r = 0.60$, $p<0.01$), extending into the pre-mining era. The lowest Hg concentrations occur prior to the Klondike Gold Rush (1896-1899). Initial Bear Creek operations mark a rise in tree-ring Hg concentrations, but this signal is small compared to a major step to peak values in the 1930s coinciding with consolidated operations. Tree-ring Hg declines rapidly after the cessation of Bear Creek operations in ca. 1966. This result suggests the principle Hg intake pathway is likely air-leaf assimilation rather than root uptake from contaminated soil, as there is no delayed decline in tree-ring Hg after the cessation of Bear Creek operations, despite a legacy of elevated soil Hg concentrations to this day. Finally, we observe that post-1966 Hg concentrations are slightly higher than pre-industrial values, likely reflecting higher global atmospheric Hg(0) concentrations. This is the first study of white spruce tree-ring Hg, and only the second to measure this variable at annual resolution. These results demonstrate that this species is a reliable recorder of local emissions, and offers great promise for longer-term reconstructions of atmospheric Hg at potentially broader spatial scales.

MP-005

MERCURY AND LEAD RECORDS IN PERMAFROST PEAT IN NORTHERN QUEBEC

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Peat cores from filled thermokarst ponds within a subarctic permafrost peatland were used to reconstruct changes in atmospheric mercury

(Hg) and lead (Pb) accumulation for the past 150 years and to distinguish between natural and anthropogenic atmospheric inputs. The study site is a permafrost peatland about 8 kilometres southeast from Kuujjuarapik, Northern Quebec. The peatland covers approximately 5 km2 at an elevation of about 110 m above sea level. The peatland is a sedge fen dotted with palsas. The study was undertaken on peat cores taken in the north-eastern part of the peatland (55.13 N, 77.41 W). The chronologies of the peat accumulation were determined using the 210Pb constant rate of supply (CRS) model in three peat cores. Temporal accumulation of mercury show up to 16 times more Hg accumulation during the mid XXth century compared to the average background mercury accumulation rate during the pre-anthropogenic period (1 g m-2 per year). Chronology of Hg accumulation is relatively similar to Pb chronology. Hg accumulation rates today still exceed the average natural background values by 4 to 5 times. Temporal variability in mercury stable isotope signatures in peat shows a clear shift between pre-industrial and industrial periods. The emission of anthropogenic Hg to the atmosphere appears to have caused variations in 202Hg and 199Hg in the uppermost layers of peatlands.

MP-006

UNDERSTANDING MECHANISMS UNDERLYING THE RATE OF RECOVERY OF MERCURY-CONTAMINATED LAKES

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Regulatory policies enacted since the 1970s at local, state and federal levels have led to considerable reduction in anthropogenic mercury emissions in the Great Lakes region of North America. Initially, reductions in mercury concentrations in biota from the Great Lakes and smaller inland lakes were apparent. More recently, however, increasing trends in Hg concentration in fish and fish-eating birds have been reported. These trends coincide with an observed increase in watershed export of organic matter, beginning in the 1990s, that may attenuate recovery of mercury-contaminated lakes. Improved understanding of the causal mechanisms driving the rate of recovery requires knowledge of fluxes of mercury to lakes from atmospheric deposition and watershed runoff.

Sediment cores were collected from five inland seepage lakes, near the University of Michigan Biological Station in Pellston, MI, that span a range of watershed area to lake area ratios (AW:AL). Concentrations of mercury in sediment profiles for all lakes show (i) a stable pre-industrial background, (ii) a pulse event associated with land clearance (logging and agriculture), and (iii) a press event associated with industrialization. In some of the lakes, mercury concentrations decline towards the sediment surface, indicating (iv) a recovery phase. Dating of sediments is in progress and will allow for, through time, the calculation of sediment mercury fluxes and the estimation of net atmospheric mercury fluxes and the additional flux of mercury delivered from watershed to lake for each unit increase in AW:AL. Measurement of natural abundance mercury isotopes in sediments from each lake for each of the four time periods will provide additional evidence of the contributions of mercury from atmospheric deposition and watershed runoff. Finally, a decadal record (1998-2008) of total mercury in event precipitation, at Pellston, MI allows for an independent record of wet depositional flux during the industrialization and recovery periods. Mercury concentration in precipitation decreased -2.02 % year-1 during 1998-2008 (Sens slope, 95% confidence intervals -3.57, 0.22, $p < 0.1$), but mercury wet deposition (flux) showed no significant trend. Our findings from the geochemical archive in combination with the decadal record of atmospheric monitoring are used to lend insight into the mechanisms controlling recovery in mercury-contaminated lakes.

MP-007

MERCURY POLLUTION IN CONNECTICUT RIVER COVES: A POINT SOURCE NEAR HARTFORD, CT?

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The Connecticut River has many narrow coves and oxbow lakes off its main channel that are partially filled with fine sediment, some displaying extremely high sedimentation rates (several cm/yr, Woodruff et al., 2013). Sediment cores from six such Connecticut River coves were analysed for total Hg, ~ 20 trace elements, organic pollutants, and dated with 210Pb-137Cs. Selected samples were analysed for Hg isotopes as a source tracer. The general spatial trend shows a typical atmospherically derived record of Hg contamination in both Barton's Cove and Oxbow Lake in Massachusetts, but much higher Hg concentrations in Wethersfield Cove at the south end of Hartford. All coves south of Hartford show Hg enrichments, reaching 2.8 ppm Hg in Hamburg Cove in the lower CT River estuary. The onset of Hg pollution is broadly dated at the early 1900s and diminishes greatly after 1970. The records from Wethersfield Cove, also an oxbow structure that formed through a cut off associated with the 1691 floods in the CT River, show pronounced Pb, Zn and Cu pollution and the highest Hg contamination of all studied coves (~3 ppm Hg). Both the Keeney Cove and Wethersfield Cove sediments show a sharp V spike in the early 1960s. Potential sources for Hg and some of the other metals are the sewage treatment plant of Hartford situated just north of Wethersfield Cove (South Meadows). In that same area a power plant was operated between 1928 and 1961 that used Hg as the working fluid instead of steam. Mercury vapour was circulated through the turbines to generate electricity, and inspection of historic company documents at the Smithsonian Museum (DC) showed severe Hg losses during the early days of operation, especially in the mid 1930s with a >20,000 lbs Hg loss. The Wethersfield Cove records show Hg peak values in the mid 1930s. Preliminary Hg isotope data show discrete changes in d202Hg over time: more negative values (<-1 ‰) for the pre-industrial Hg and d202Hg values ~ -0.5‰ for post-industrialization. Peak Hg loadings to the sediments in Oxbow lake, Keeney Cove and Hamburg Cove are associated with the highest d202Hg values, suggesting a "pollution end member" with d202Hg close to ~ 0‰.

MP-008

TREE RINGS AS A VALUABLE ARCHIVE OF ATMOSPHERIC HG EMISSIONS? HYPOTHESIS TEST UNDER THE CROSS-FIRE OF EMISSIONS FROM GOLD AMALGAMATION

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The value and evidence potential of the tree ring archives as a proxy for changes of atmospheric Hg pollution is still not overall accepted and appreciated. In this work, we present a proof advocating for acceptance of this archive, comparing tree ring Hg record in larch (Larix decidua) against known history of Hg emissions from Roudný gold mining site in the Czech Republic, central Europe. The period of large scale mining at Roudný started 1904 and ceased in 1930. The amalgamation technique was used for the gold ore extraction and amalgam was decomposed at an in-site laboratory with distilling equipment. Nevertheless the losses of Hg during amalgam decomposition amounted at 5-7 g per ton of processed ore. Gold extracted from 664 400 tons of processed ore amounted at 5700 kg. The annual records of gold mined and Hg lost during the extraction process are available for estimate calculation. Besides that, period 1900-2016 is covered by the life span of a currently growing larch trees.

We sampled tree ring cores of four 120-140 years old larch trees at a distance of 32, 88, 275 and 313 m from the amalgamation laboratory. The most significant record of Hg emissions was in the closest tree 32 m from Hg emission source. Its tree rings in sections corresponding to the period between 1905 and 1931 were typical with the highest Hg concentrations up to 41 μg/kg. While Hg concentration in tree rings before and after operation of laboratory averaged at 4.3 μg/kg. The relationship of the peak Hg concentrations in the tree-rings to the peak usage of Hg in amalgamation demonstrates that the Hg record within the bole has been preserved. No signs of significant mercury migration into the heartwood have been noticed as claimed by some previous studies.

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MP-009

MERCURY RECORDS FROM BLOCK ISLAND, RI: 600 YEARS OF ATMOSPHERIC HG DEPOSITION IN A REMOTE LOCATION

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Regional Hg atmospheric deposition records in southern New England are often impacted by local sources. Block Island, RI, is a small glacial relic island just south of the Rhode Island coastline. Its many seepage lakes and ponds have almost no drainage basins, and Block Island has no industry and sparse population. We therefore expected Block Island sediment records would capture local atmospheric Hg deposition with little interference from other sources or watershed sediment focusing. We analysed 14 sediment cores for Hg and then focussed on Fresh Pond and a freshwater marsh near West Beach. These cores were analysed for total Hg, dated with 210Pb-137Cs, 14C, and pollen methods. From sedimentation rates and bulk dry densities we calculated Hg accumulation rates and standing inventories for Hg and 210Pb. Pre-industrial concentrations were 30-40 ppb Hg, whereas concentrations in the mid 20th century were up to 320 ppb Hg. The Hg accumulation rates increased from 2 ng Hg/cm2 yr to 18 ng Hg/cm2 yr in the mid 20th century. Some cores show a clear decrease in Hg over the last 35 years. The Hg - 210Pb inventory ratios vary slightly for the two locations, indicating some sediment focussing, largely from aeolian transport. Both records show gentle increases in the mid to late 1800s, but then a strong increase starting around 1940. The modern Hg accumulation rates are of the same order as measured regional bulk Hg deposition rates. Long Island Sound sediment cores show the start of strong Hg contamination in the mid 1800s, and no clear change in slope at 1940. These contamination records are dominated by local Hg sources, especially Hg pollution from the Western Connecticut hat making industry, and also have higher Hg-210Pb inventory ratios. The early part of the Block Island record (1400-1600CE) is characterized by natural background values only. Evidence for atmospheric Hg pollution associated with the early colonial era silver and gold mining by the Spanish in S-America is absent. The magnitude of Hg releases from these colonial mining operations would lead us to expect anomalous Hg values during this era (1500-1700 CE). This missing Hg is either the result of local retention of the mining Hg or emission of Hg species that were rapidly removed from the atmosphere.

MP-010

DO CHANGES IN FOREST VEGETATION CHANGE MERCURY ACCUMULATION IN LAKE SEDIMENTS? - A CASE STUDY FROM THE BLACK FOREST (GERMANY)

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Forest vegetation plays a key role of the cycling of mercury (Hg) in terrestrial ecosystems and litterfall has been indicated to be the major transport vector of atmospheric Hg to forest soils. Soil organic matter (OM) is the dominant carrier of Hg from catchment soil to lake sediments. Hence, it is important to understand how changes in forest vegetation affect Hg in soil and its biogeochemical cycling in lake systems. To evaluate whether long-term shifts in forest vegetation induced by climate- or land-use changes influenced Hg-accumulation in lakes we investigated a sediment record from a cirque lake (Glaswaldsee) located in the Black Forest (Southern Germany). We were particularly interested if coniferous vegetation leads to a larger export of Hg to aquatic systems than deciduous vegetation. The radiocarbon-dated sediment core shows a well-defined Holocene vegetation history based on pollen-analyses. The forest vegetation during the Mesolithic at the Glaswaldsee was dominated by Corylus avellana (hazel) until ~ 7800 year BP. Hazel was replaced by Quercus robur (oak), which was replaced at ~ 5400 years BP by a mixed forest of Abies alba (fir) and Fagus sylvatica (beech). When oak replaced hazel, there was neither a significant change in mean Hg-concentration (~ 117 ng g-1) nor a shift in Hg:C ratio. However, Hg-concentrations increase to 198 ng g-1 directly after the appearance of fir and beech. Nevertheless, there was no substantial increase in Hg-accumulation rates because the increased Hg concentrations were caused by decreasing input of OM through litterfall in coniferous forest resulting in higher Hg:C ratios. At around 1270 years BP an additional increase in Hg concentrations in the Glaswaldsee sediments was observed, which might be due to an increasing in atmospheric fluxes attributed to increasing human activities e.g., forest clearance or mining. Hg concentrations peak (640 ng g-1) around 650 years BP when deforestation was highest. Our results contrast earlier studies that suggest an inevitable higher release of Hg from coniferous than deciduous forests.

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MP-011

THE ISOTOPIC COMPOSITION OF HG-ENRICHED MARINE SEDIMENTS: A GEOLOGIC PERSPECTIVE

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In the modern world, primary and legacy anthropogenic Hg emissions account for most of the Hg released to Earths atmosphere and dwarf the contribution of Hg from natural sources (e.g. volcanoes). However, there are intervals in the geologic past where natural processes, such as massive volcanism, likely emitted of large amounts of Hg to Earths atmosphere at rates comparable to human activities. Evidence for enhanced Hg emissions in the geologic past is recorded in marine sedimentary rocks, which contain global-scale spike(s) in their Hg contents and/or Hg/TOC ratios (i.e., Hg anomalies) coincident with periods of prolonged, large-scale volcanism. Here, we examine the Hg stable isotopic composition of marine sediments deposited during times of massive volcanism, drawing both from our own work on Triassic-Jurassic Hg anomalies and the broader literature. In particular, we provide evidence that, over the past several hundred million years, the isotopic signature of near-shore sediments has been more sensitive to changes in Hg-loading and Hg cycle perturbations than deeper-water sediments. Investigating the isotopic composition of marine sediments deposited before, during, and after these ancient Hg-loading events provides a geologic context for understanding the sources and pathways of anomalous Hg deposition to the oceans and supplies insight into the ways that anthropogenic Hg emissions may alter the Hg isotopic ratios of modern marine sediments.

MP-012

ANTHROPOGENIC HG DEPOSITION HISTORY AND INVENTORIES NEAR POINT SOURCES AND IN REMOTE REGIONS USING MULTI-LAKE SEDIMENT CORE RECONSTRUCTIONS

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The monitoring record of atmospheric Hg content and deposition is both brief and natural as well as anthropogenic Hg emission estimates have considerable uncertainties. Paleo-reconstructive methods are needed to determine the historical and natural deposition rates of Hg and a wide variety of other contaminants as well as help constrain modeling of contemporary atmospheric processes of Hg deposition and cycling between reservoirs. As part of the Government of Canadas Clean Air Regulatory Agenda (now Climate Change and Air Pollutants) program we have been trying fill in knowledge gaps regarding Hg deposition history and inventories on the Canadian landscape near major point sources and in regions remote from population and industrial centres using multi-lake sediment core reconstructions. The aim of which is to

produce quantitative spatial and temporal Hg deposition data spanning pre-industrial times through to the modern day, tracking the onset of Hg emitting industries and the post regulation period comparing with contemporary monitoring data where possible. Multiple lake coring sites within a region serve as multiple receptors producing a coherent landscape signal after accounting for site specific natural Hg background conditions, changes in sedimentation rates and sediment focusing. The combined signal from multiple lake sediment cores helps remove residual site specific biases and can be used to develop a temporal-spatial distribution of Hg inventory deposited on the landscape with respect to a major point source which can be compared directly with long-term estimated emission inventories from the point source. Here we present some preliminary data collected from lake sediment cores in a region isolated from industry (Kejimkujik National Park Nova Scotia, Canada) and lake sediment cores collected various distances from the Pb-Zn smelter in Trail British Columbia, Canada which has been in operation for more than a century. As Trail is situated on the Columbia River 11 km from the US-Canada border it has given rise to in some of the earliest transborder pollution disputes in North America.

MP-014

UNDERSTANDING HISTORICAL CHANGES OF MERCURY OVER THE TIBETAN PLATEAU WITH A STRATEGY OF MULTIPLE MEDIA AND TECHNIQUES

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The Tibetan Plateau (TP) is located in the Central Asia and represents the highest and remotest landform on the earth. It is distant from point sources of mercury pollution and is relatively isolated. It is endowed with various environmental matrices such as glaciers, rivers and lakes, serving as a unique place for understanding the cycling of mercury and its history. Reconstructed time series of Hg deposition from ice core and lake sediments showed consistent patterns along with the Asias mercury emission. However, the rough resolution of lake sediments and the loss of recent glacial records preclude detailed insights into recent changes in mercury over the TP. Active monitoring of atmospheric mercury started from ~2010 at sporadic sites (e.g., Waliguan, Nam Co, and Everest) reported TGM of~1-2 ng/m3, which agrees well with the background of Northern Hemisphere. A combination of passive air sampling and biomonitoring of a native plant (Androsace tapete) in the central TP revealed a general decline of atmospheric mercury since ~2010.

Single environmental medium or monitoring technique can record mercury changes with respective advantages and limitations. For example, lake sediments can yield long term records (hundreds to tens of thousands of years) but has low resolution (5-10 years). Glacial ice cores span thousands of years with seasonal to annual resolution, however, ice core mercury records are sometimes questioned due to active mercury mobility in the interface of snow-atmosphere. Active mercury monitoring is accurate but only covers very recent years and is deficient. We suggest undertaking intercomparison, integration, and reconciliation of historical mercury records and measurements from diverse natural archives and monitoring techniques, to reveal a larger and more detailed view of mercury changes over the TP.

MP-015

LATE HOLOCENE MERCURY DEPOSITION HISTORY IN LAKE CHUNGARÁ (4500 M A.S.L., CHILE): INFLUENCE OF VOLCANIC ERUPTIONS AND CHANGES IN PALEOLIMNOECOLOGY.

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Lake Chungar is the largest and deepest lacustrine ecosystem in the Chilean Altiplano located in the active volcanic setting of Parinacota (6348 m a.s.l.). The late Holocene period is characterized by intense volcanic activities resulting in the deposition of numerous tephra layers followed by a gradual decrease of volcanic activity which stopped around ~500 cal yr BP. Two sediment cores collected in Lake Chungar (4500 m a.s.l.) were analyzed in high-resolution (mm to cm scale) to provide mercury concentration (Hg) profiles together with X-ray fluorescence (XRF) geochemical parameters (e.g., K, Fe, Si) and molecular composition of organic matter (OM) determined by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). Our high-throughput Py-GC/MS method yielded semi-quantitative data on 86 organic compounds belonging to different biochemical classes of OM (e.g., carbohydrate, lipid, chlorophyll). The combination of inorganic and organic geochemical properties allowed us reconstructing the Hg deposition history and mechanisms with regard to the volcanic, limno-ecological and anthropogenic history of the region during the last 3,000 cal. yr BP.

Results highlight that volcaniclastic layers (~ 12) are characterized by abrupt rises in dark mafic mineral enriched in Fe and K accompanied with a strong decrease in Hg concentrations and in the abundance of organic compounds associated to plant and/or algal production (e.g., carbohydrates, proteins and chlorophylls). This is followed by abrupt rises in Hg and in abundances of carbohydrates, proteins and/or chlorophylls. Such feature demonstrates the rapid deposition of coarse volcanic minerals impoverished in Hg followed by a post-eruption deposition of Hg due to atmospheric oxidation of Hg and its recycling by lake biota (i.e., mostly phytoplankton) which recovers from the eruption.

Finally, for the last 500 years of our record, Hg exhibited a sharp rise associated with Ag mining activities during the Colonial era (15541900 AD), followed by a Hg steady decrease illustrating lower Hg inputs during the twentieth century although they remain elevated relative to the pre-industrial background.

MP-016

SOLAR INSOLATION AND ALGAE PRODUCTIVITY CONTROLLED MERCURY ACCUMULATION IN THE PAST 5 KYRS IN A PRISTINE LAKE IN THE SOUTHERN HEMISPHERE

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Mercury (Hg) highly accumulates in aquatic biota and uptake by algae has been found to be its entry-point into the aquatic foodchain, but the contribution of Hg uptake by algae under changing solar irradiance and climatic conditions has not yet been investigated for pre-industrial times. We analyzed the link between Hg accumulation, cyclic changes in total solar insolation (TSI), related changes in productivity and climate during the past 5 kyrs in sediments of a small highly productive lake located in Southern Patagonia (53°S). Analyzes encompass proxies for solar irradiance (TSI based on 10Be), sediment geochemical composition and lake productivity (FTIR spectra, and hydrogen-index (HI)).

The sediment record shows high accumulation of organic matter (median 70 %) and strong variations in Hg accumulation which correspond to changes in TSI and productivity. Accumulation of Hg was highest during drier periods when insolation and lake productivity was high and erosion fluxes from the catchment were low. This indicates that sediment Hg accumulation and potential methylation in this highly productive lake are to a large extent controlled by insolation and related algae production and to a lesser extent by direct atmospheric deposition and Hg fluxes supplied by erosion from catchment soils. We suggested that the high Hg uptake by algae is attributed to oxic water-column methylation in settling patticles in anaerobic micro-niches at times of high productivity. Hg accumulation during periods of high TSI and lake productivity were on an avergae threefold higher compared to periods of lower TSI and productivity and wetter conditions. Our findings suggest that sediment Hg accumulation releated to increased TSI, water phase methylation and algae uptake can surpass Hg fluxes from the catchment in productive lakes.

1i: Comparable measurement results for mercury analysis and speciation

TO-006

SELECTIVE SEQUENTIAL EXTRACTION OF MERCURY IN HIGH LEVEL RADIOACTIVE WASTE

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The liquid waste system at the Department of Energy's Savannah River Site contains an estimated 60,000 kg of mercury in both salt cake and insoluble metal oxide/hydroxide solids (sludge). Inorganic mercury was used as a catalyst to aid in the dissolution of aluminum clad fuel and target assemblies associated with separation processes that supported the United States nuclear stockpile. For long-term storage and disposal the radioactive liquid waste is being converted into a solid glass form using a vitrification process. This process immobilizes the radioactivity within a solid glass phase matrix. The baseline assumption employed for radioactive waste sludge used in the vitrification plant has been that incoming mercury is present only in the form of mercuric oxide. Recent findings from other components of the liquid waste system have unveiled a considerable amount of methylmercury in the system, along with inorganic mercury, elemental mercury, dimethylmercury, and particulate mercury. These discoveries have challenged the validity of the assumption regarding mercury oxide as the only species in the insoluble sludge component.

The focus of this study was to develop and apply a modified selective sequential extraction (SSE) technique to characterize mercury species that are present in the highly radioactive insoluble sludge component of the liquid waste system. Sequential extraction is a proven analysis technique often used with environmental solid samples, typically soils. Due to the highly radioactive nature of the sludge samples, all manipulations of the material were conducted in the Shielded Cells Facility that is located at the Savannah River National Laboratory using remotely controlled master-slave manipulators. The remote application of the extractions required modification of the established SSE techniques. The insoluble sludge solid extractions were compared to Kaolin Clay standards containing mercurous chloride, mercuric oxide, and mercuric sulfide that were processed in parallel with the radioactive insoluble sludge solids. The clay standard extracts, diluted samples of the sludge extracts, and diluted supernate were shipped to Eurofins Frontier Global Sciences for mercury measurements. Prior to shipment, dilution of the extracts was necessary to reduce the radioactivity of the shipped samples. Results from these extractions will be presented along with the implications for process development activities within the liquid waste system and recommendations for future study.

MP-017

MERCURY SPECIATION BY PYROLYSIS-THERMO-DESORPTION AND HG ISOTOPE SIGNATURES BY CV-MC-ICP-MS IN METEORITES

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Mercury is a highly volatile element and a potentially useful tracer for cosmochemical studies, but the controls on Hg concentration and speciation in meteorites are poorly understood. Previous studies reported surprisingly large variations in Hg concentrations (~101–104 ppb) that did not follow the general volatile depletion trend of other elements. Some studies proposed terrestrial contamination as the origin for the high Hg concentrations, while others argued against this explanation. A key factor to solve this conundrum is the form, in which Hg occurs in meteorites. In addition, mass-dependent (MDF) and mass-independent fractionation (MIF) of stable Hg isotopes can provide additional constraints on the origin and modification of Hg in meteorites.

Here, we present data from three different meteorite groups (ordinary and carbonaceous chondrites, eucrites). Concentrations were determined by combustion AAS, isotope ratios by CV-MC-ICP-MS on acid digests and/or after pre-enrichment using a dual-stage combustion oven, and Hg species by pyrolysis--thermo-desorption-AAS (PTD), in which the Hg release was continuously recorded up to 700°C under N2 gas flow. A wide range of Hg concentrations from 2.8 ppb (NWA 2714) to 88420 ppb (Orgueil) was found without systematic trends with meteorite class. MDF (δ202Hg) relative to NIST-3133 varied from -3.55‰ (Orgueil, CI) to +0.14‰ (Bouvante, eucrite), but no systematic trends with Hg concentration or meteorite class were apparent. Small but resolvable MIF (Δ199Hg) was observed from -0.07‰ (Bouvante) to +0.15‰ (Orgueil) with a negative correlation between δ202Hg and Δ199Hg. This is a typical feature for MIF caused by the nuclear volume effect.

All TD Hg release curves of ordinary chondrites showed a uniform single peak maximum temperature between 180 and 200°C. Based on comparison with Hg(0) incubated minerals, this may indicate the release of metallic Hg trapped in pores of the mineral matrix. TD measurements of carbonaceous chondrites present a more nuanced picture: Orgueil shows two distinct release peaks at ~200 and ~280°C representing 40% and 60% of total Hg release, respectively. In contrast, Allende and Vigerano yielded a main peak with an extinction maximum at 180-190°C and a small peak shoulder at ~230°C. The first Orgueil peak falls between standards of Hg(0) adsorbed on Fe(OH)3 and β-HgS (metacinnabar). The second Orgueil peak appears slightly earlier than our α-HgS (cinnabar) standard, which could indicate the presence of microcrystalline α-HgS. Our data on Hg concentrations, species and isotopic variations in meteorites argue against terrestrial contamination and provide new constraints for cosmochemical studies.

MP-019

AN ALTERNATIVE ANALYTICAL TECHNIQUE FOR MERCURY SPECIATION IN RADIOACTIVE TANK WASTE AT THE SAVANNAH RIVER SITE

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Significant levels of mercury (Hg) are present in the underground storage tanks at the US Department of Energy Savannah River Site, and removal of the Hg from the radioactive liquid waste stored in these tanks is a major concern and challenge. The species of Hg in the tank wastes are suspected to have changed over time, resulting in changes in the stabilization efficiency of Hg in the solid waste products (e.g., Saltstone). It was originally believed that the Hg in the tank wastes was present primarily as HgO and Hg(II). Increasing Hg concentrations from leachate characterization testing (TCLP) of the saltstone triggered an investigation. Initial testing of the saltstone waste feed showed a significant amount of organomercury species. As individual tanks were further tested, poor mass balance was often observed between the total Hg concentration and the sum of the Hg species that were measured, resulting in ambiguous data interpretation. Since the efficacy of the treatment process is dependent on the molecular forms of Hg present in the waste, the site contractors investigated whether alternative analytical techniques would yield a better mass balance.

Diluted tank waste samples were analyzed for total Hg, dissolved Hg, inorganic Hg, elemental Hg, methylmercury, ethylmercury, and dimethylmercury by Brooks Applied Labs (BAL) using methods based on CV-AFS technology, which have been in use for many years. BAL also developed alternative analytical techniques for the simultaneous analysis of inorganic Hg, methylmercury, ethylmercury and phenylmercury using ion pairing chromatography with cold vapor generation and inductively coupled plasma mass spectrometry detection (IP-CV-ICP-MS) and dimethylmercury by reverse phase chromatography (RP-ICP-MS). Additionally, methylethylmercury and diethylmercury reference materials were prepared as quality control standards. Results from the two methods are compared and discussed.

MP-020

A COMPARATIVE ANALYSIS OF GOM MEASUREMENT USING TWO METHODOLOGIES AND ENVIRONMENTAL CORRELATES IN AN URBAN SETTING IN AUSTRALIA.

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Accurate quantification of atmospheric mercury (Hg) concentrations are critical for understanding the Hg biogeochemical cycle and for the development of effective policy and management. However, a number of recent studies have revealed uncertainties in the accurate measurement of gaseous oxidised mercury (GOM), where biased low measurement has shown to occur with the use of KCl-coated annular quartz denuders traditionally used for atmospheric GOM measurement. Additionally, there is also evidence to suggest that environmental parameters affect the accurate quantification of GOM, including relative humidity and tropospheric ozone (O3) concentration. In this study, we present a method comparison between KCl-coated annular quartz denuder based methods and a novel method which utilises cation exchange membranes and nylon membranes to measure total GOM and differentiate GOM species. We additionally explore the dependence of GOM on environmental variables, and investigate the variables which control GOM events. This study presents the first of its kind within the Southern Hemisphere, and is undertaken at an urban site in Sydney, Australia, from the period April 2016 onwards. Mean background concentrations at this location as determined by the UNRARM system are 20.2 pg m-3, and 5.4. The findings from this study aim to assist in the development of more accurate GOM sampling methodology, as well as providing a greater understanding of the ways in which environmental parameters influence GOM measurement.

MP-021

AN SI TRACEABLE MERCURY VAPOUR CALIBRATION FACILITY FOR THE 5 NG – 55 µG HG/M3 RANGE

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Within the EMRP (European Metrology Research Programme) project "MeTra" a mercury vapour generator is being developed to establish SI traceability for mercury vapour measurement results in the range from 5 ng Hg/m3 up to 55 µg Hg/m3.

The novel calibration facility generates a tuneable mercury vapour directly traceable to primary mass standards. The facility can be used for the calibration of mercury monitors as well as for the loading of sorbent traps.

The facility consists of a modified type of diffusion tube, a new measurement method to weigh the loss in (mercury) mass of these diffusion tubes during use (with a minimum 6-8 µg mass difference between successive weighings), and a new housing for the diffusion tubes to optimize flow characteristics and to minimize temperature variations and adsorption effects.

The specifics of the newly introduced capabilities, to calibrate mercury monitors at levels of 5 ng Hg/m3 and higher, will be highlighted. This new calibration service is especially important for measurement services testing ambient air monitoring (1 – 2 ng Hg/m3), indoor and work place related mercury content levels according to health standards (from 50 ng Hg/m3) as well as mercury vapour concentrations relevant to stationary source emissions (upwards of 1 µg Hg/m3).

MP-022

SIMPLIFIED METHOD FOR DETERMINATION OF MONOMETHYLMERCURY (MMHG) IN SEDIMENT/ SOIL SAMPLES BASED ON SEPARATION OF HG DITHIZONATES AND CV AAS DETECTION

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Measurements of MeHg in sediment and soil samples represent a challenge. This is due to the nature of the matrix, high ratio between inorganic mercury (Hg) and MMHg and risks of artefact MMHg formation during extraction and measurement procedures. The latter is of particular concern due to the high inorganic Hg presence in sediments. Simple extraction method for quantitative separation of MMHg from inorganic mercury has been developed.

The method consists of alkaline leaching with 1N KOH in ethanol from a sediment (usually 0.2-0.5 g of wet weight and 0.2 g of dry sample) followed by addition of NH2OHHCl and EDTA-4Na. Sample is then slightly acidified with 1N HCl and purged with nitrogen gas to remove possible S2+ ions as H2S. The next step involves derivatisation by dithizone and quantitative extraction of both MMHg and inorganic Hg dithizone complexes into toluene. Hg(II) and MMHg dithizonates are then separated on silica gel column and selectively collected into separate test tube. The collected sample is evaporated to dryness and digested with mixture of acids (HNO3/HClO4 and H2SO4) and measured by CV AAS. The limit of detection and limit of quantification are 0.2 ng/g and 0.67 ng/g, respectively.

Separation of inorganic and organic mercury is quantitative, independent on inorganic mercury content and absence of artefact MMHg formation. The method was validated using certified reference materials (CRMs).

Compared to other methods this method is simple and inexpensive from the point of view that the instrumentation which is used for total mercury measurements can be used to measure organic mercury. The detailed analytical methods as well as the comparison of MMHg in various sediment samples between conventional methods and newly developed method will be presented.

MP-023

CAN FORMALIN-PRESERVED ZOOPLANKTON SHED LIGHT ON TEMPORAL PATTERNS OF METHYLMERCURY BIOACCUMULATION?

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Changes in climate, global and local mercury emissions into the environment may influence the cycling of methylmercury (MeHg) and its bioaccumulation in marine organisms. Following the decrease of atmospheric Hg emissions or discharge into rivers a decline in biota MeHg concentrations is expected. Analysis of historic biota samples for their MeHg concentrations could offer a pathway to unravel temporal patterns. Because copepods are a strong link between primary producers and upper trophic levels it is important to better understand their MeHg bioaccumulation. There is a vast depository of biological samples preserved in formalin, but it is unclear if these samples can be used for MeHg measurements. We tested for temporal changes of MeHg concentrations in formalin-preserved copepods. Because the life span of many copepod species is on the order of a weeks to months, and MeHg that is highly assimilated (>90%) is lost very slowly, copepod MeHg represents recent cumulative exposure. We tested the null hypothesis that formalin preservation does not influence MeHg concentration in copepods over time. We collected two copepod species Acartia tonsa and Temora longicornis from a local embayment in Connecticut, US. These species were selected to represent smaller and larger size classes of copepods found in coastal embayments. Copepods (n=3 replicates of 50 individuals) were picked prior to formalin preservation and stored frozen on a polycarbonate filter. The remaining copepods were preserved with formalin for time intervals e.g. 1 week, 1 month, 6 months and up to a year. At the end of each preservation period, copepods were filtered via polycarbonate filter and kept frozen prior to analysis. Filters with copepods were acid-digested and analyzed for MeHg by direct ethylation of digest aliquot diluted in deionized water. Initial values were 0.20 pg per an individual for the small copepod, A. tonsa (average prosome length or PL: 0.9 mm) and 0.30 ng per copepod for the larger T. longicornis (average PL: 1.2 mm). MeHg concentrations dropped to ~ 25% of initial values within two weeks (T. longicornis) to a month (A. tonsa), and subsequently increased by a factor of ~7 within 6-12 months for A. tonsa and 1.5 for T. longicornis. The mechanism for these dramatic increases has not been tested yet. Additional research on abiotic MeHg formation during formalin incubation is needed.

MP-024

HG COMPOUND SPECIFIC STABLE ISOTOPE ANALYSIS (CSIA) AT ULTRA-TRACE LEVEL USING AN ON LINE PRE-CONCENTRATION AND GC SEPARATION STRATEGY HYPHENATED TO MC-ICP-MS

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Stable Hg isotope analysis is now widely used in environmental sciences, essentially for discriminating Hg sources and better understanding its bio-geochemical cycle. Up to now, total Hg isotopic composition has been mainly studied. Further, the compound specific Hg isotopic analysis (CSIA) is an emerging tool providing the isotopic signature of each different Hg species such as inorganic Hg (InHg) and methyl Hg (MeHg). However, one of the main challenges remains the low Hg concentration in most environmental compartments. In this work, we propose to overcome this limitation using an on line Hg pre-concentration strategy combined with gas chromatography (GC) hyphenated to MC-ICP-MS. The GC is here fitted with a programmable temperature volatilization (PTV) injector and a liner filled with a specific solid phase. This allows the injection of a large volume of sample (up to 100 times larger than conventional injector) and a pre-concentration of the Hg species in the liner before their separation and detection. The pre-concentration and separation parameters such as the inlet and GC temperature during the injection phase, the gas flow and duration of the venting period, were first optimized using a regular quadrupole ICP-MS instrument. When transferring the method to MC-ICP-MS, the main challenge was to deal with very short transient signals (down to 11 s) and this aspect was solved using a suitable data treatment strategy. Contrary to previous GC/MC-ICP-MS methods, we also demonstrated that our method required a compound specific standard bracketing procedure due to the nature of the pre-concentration involved.

The main advantage of the proposed methods is the high pre-concentration capability which allows the compound specific isotopic analysis with InHg or MeHg concentrations down to 50 ng.L-1 in liquid matrices and 200 ng.g-1 for solid samples (after extraction). At this level, the method gives a good accuracy and a maximum uncertainty of 0.30‰ (as 2SD) for both δ and Δ.

We will discuss the main advantages and limitations of the proposed method, such as the potential pre-concentration capabilities and associated limits in term of Hg concentration. We'll also present the critical steps of technical validations including the analysis of environmental CRMs and comparison to the actual reference technique.

MP-025

ATTAINING A LABORATORY REFERENCE MATERIAL FOR THE ROUTINE MEASUREMENT OF METHYLMERCURY IN RICE.

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Rice is a staple food for many countries around the globe, but it is also known to accumulate MeHg the most toxic mercury species to humans. Therefore, accurate determination of this species in rice ismandatory. However, while a certified Reference material (CRM) exists for total Hg in rice,there is noCRMfor MeHg in a rice matrix. In earlier work, we could show that the % of MeHg in rice can vary substantially. Therefore, we aimed tocreate alaboratory reference material(LRM) for our purposes,in order toassess theperformance ofroutine measurements.Onekg of long grain white rice was purchased from a local supermarket and ground into a fine powder and mixed well. It was thenanalysedrepeatedly,using a TMAH/HCl digestion followed bypre-concentration CV-AFS.MeHg and Hg2+were separated by RP-LC and on-line chemical oxidation and reduction with acidified Br-/BrO3-and SnCl2was used prior to AFS detection. This method hasbeen proven to be accurate and precise by cross-calibration using species specificisotope dilution mass spectrometry.

For the determination of precision and accuracy, the rice powder was split into several sub-sets andanalysed repeatedlyto assess variation between the sub-sets. The measurement of the samples gave a concentration range between 3.05mg kg-1and 3.68mg kg-1, averaging at 3.36mg kg-1. Further analysis will include the testing of the materials shelf-life.

MP-026

PECULIARITIES OF MERCURY DISTRIBUTION IN COALS

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Coal is apt to concentrate mercury and other toxic elements whose content is governed by geological and geochemical specificity of the coal basins. The mercury concentration in coal varies in a wide range from < 1 ppb to 300 ppm. Metamorphism and subsequent hydrothermal processes generate different mercury species in coal and in coal-bearing strata. The mercury species having different matrix binding energy can be determined by thermospeciation technique based on the study of mercury release from a sample during its gradual heating. Total mercury concentration and mercury thermospeciation in coal were determined using RA-915M Zeeman atomic absorption spectrometer. We studied features of the mercury distribution in samples of brown and hard coals with different metamorphism degree of the organic matrix.

Total mercury concentration in the studied coal samples lies in a wide range of less than 2 to 7600 ppb. The thermoscanning reveals various mercury thermospecies in coal. The low-temperature peaks, below 200 OC, can be attributed to mercury bound by physical sorption, and the mid- and high- temperature peaks to mercury bound to organic coal matrix, sulfides (mainly pyrite), and silicates. Low-temperature forms of mercury evaporating at 240-350 OC prevail in brown coal. The most high-temperature species releasing at 640 900 OC were found in shungite.

The scanning electron microscopy and electron probe microanalysis reveal peculiarities of mercury and other chemical elements distribution in organic matrix and inorganic impurities. The mercury accumulation in coals was found in organic matrix, sulfides, iron oxides and hydroxides, clay minerals and phosphates. The scanning electron microscopy helped us to identify the following terrigenous minerals within coal matrix: quartz, potassium and sodium feldspars, hydromica, kaolinite, chlorite, rutile, apatite, and sphene. Correlation analysis has shown that the mercury concentration correlates with the elements of the halophile group: Fe, Mo, Ag, Ni, Zn, Sb, Cu. Correlation coefficients vary from 0.74 to 0.94. Mercury has significant correlation with V, Ge, K, and Al, which can be explained by the effective mercury Hg(0) sorption by clay minerals; this finding is supported by the thermoscanning data.

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MP-027

TESTING THE EFFECTS OF WIND SPEED, HUMIDITY, AND TEMPERATURE ON THE SAMPLING RATE OF A PASSIVE AIR SAMPLER FOR GASEOUS MERCURY

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We recently developed a passive air sampler (PAS) for gaseous mercury, and determined a sampling rate (SR; defined as the volume of air stripped of analyte per unit time) of 0.121 ± 0.005 m3 day−1 in a year-long, outdoor calibration in a temperate environment. A model based on Fick's First Law of Diffusion predicted a SR within 10% of this calibrated value. Here, we present results from a series of controlled laboratory studies that tested the potential impacts of variable wind speed, relative humidity, and temperature on the SR of the PAS. We find a logarithmic relationship between wind speed and SR, with the greatest impacts at wind speeds less than 1 m s-1, which are not common for outdoor deployments. When we consider only data from wind speeds between 1 and 6 m s-1 we find a significant positive linear relationship ($p < 0.001$), indicating a 0.003 m3 day-1 increase in SR (corresponding to 2.3% of the previously calibrated SR) for every m s-1 increase in wind speed. Similarly, SR increases linearly with temperature in the range -15 to +35°C ($p < 0.001$). This temperature dependence can be fully explained by the effect of temperature on the molecular diffusivity of gaseous mercury in air, which is calculated to lead to a 0.008 m3 day-1 increase in SR (6.9% of the calibrated SR) per 10 K increase in temperature. SR is not significant affected by relative humidity, tested between 44 to 80% at 20°C ($p = 0.08$). While differences in SR caused by wind speed and temperature are relatively small, the accuracy of passively sampling gaseous Hg in air can be improved by adjusting SRs using the slope of the relationships described here, if measured or estimated temperature and wind speed data at or near sampling sites are available.

MP-028

QUALITY-SCREENING FOR ATMOSPHERIC MERCURY DATA WITHIN THE GMOS NETWORK

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In response to the increasingly severe issue of mercury pollution, the EU funded Global Mercury Observation System (GMOS) project (FP7) established a global monitoring network, that in the last five years provided harmonized and detailed information on mercury ambient measurements through a dedicated database platforms (www.gmos.eu). Among others, the atmospheric mercury data obtained from the GMOS network has become an essential data source for many current and forthcoming studies as well as for the formulation and implementation of the Minamata regulatory policies. In respect to data management, within this project an ad-hoc centralized system, namely GMOS-Data Quality Management (G-DQM), was developed and used to release high-quality atmospheric mercury data collected with the Tekran speciation instrument. Based on a web application, the system is able to fulfil the demands of processing monitoring data in near real-time, verifying if instruments adhere to standard procedures, and rapidly identifying non-representative measurements. The use of automated common checks represents an improvement because it ensures consistency and reduces human bias thus avoiding misinterpretation and inappropriate data use. Despite the wide use of the Tekran speciation system, recent studies increasingly acknowledge that the atmospheric reactive mercury species, Gaseous Oxidized Mercury (GOM) and Particle-Bound Mercury (PBM), have large measurement uncertainties. Besides that, in our study we want to elucidate how significant are the quality control issues and identify how much they-self can additionally affect the resulting validated datasets. Referring to 2013 and 2014 years, during which we had a good coverage of speciation data for 7 GMOS Master stations, at the end of the whole validation process we were able to discriminate between valid and invalid speciated data. For both the years, we had an average percentage data loss of about 30%. The incidence of rejected data, in terms of discrepancy from the final quality-validated concentrations was, on annual basis, in the range from 0.02 to 4.89 pg.m-3 for PBM, and from -0.79 to 3.11 pg.m-3 for GOM, respectively. In terms of monthly means, we obtained a larger gap ranging from -0.46 to 40.23 pg.m-3 for PBM and from -0.79 to16.40 pg.m-3 for GOM, respectively. Based on GMOS monitoring data, this work thus intend to highlightthat quality control issues could significantly affect the resulting atmospheric mercury data. Furthermore, it suggests that researchers using data from any source be expected to manage data with due caution depending on the fact that they are or not quality controlled.

MP-029

EVALUATION OF FACTORS AFFECTING THE USE OF DRIED BLOOD SPOTS FOR MERCURY EXPOSURE ASSESSMENT

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Dried Blood Spots (DBS) are drops of whole blood collected on standardized paper from a finger or heel prick. They have been used since the 1960s for newborn screening programs, pharmacokinetics studies, and demographic health surveys. The use of DBS for the analysis of mercury exposure in newborns has been studied previously in two studies, although both suffered from poor detection limits and challenges with accuracy and precision. Challenges in measuring mercury in DBS (as supported by the European Bioanalysis Forum) include: 1) the impact of hematocrit levels on analyte and spot formation; 2) differences between measures taken from venous and capillary blood; and 3) matrix effects. Therefore the objective of this study is to evaluate whether total mercury and methylmercury content in DBS differs between blood sources (venous or capillary), and hematocrit levels. Whole blood and DBS from venous and capillary sources were obtained from 49 healthy individuals associated with McGill University (Canada). Total mercury in the blood and DBS will be determined by acid digestion and by Dual-Stage Gold Preconcentration, and methylmercury by tetramethylammonium digestion and Gas Chromatography (GC) - Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). Initial blood analysis showed no significant difference in hematocrit levels between venous and capillary blood, although a range of other clinical blood parameters are under investigation. We are currently in the midst of analyzing all samples for mercury. The results are expected to increase our understanding of DBS as a potentially novel means to assess mercury exposure. This could have immediate applications in established programs such as newborn screening and demographic health surveys.

MP-030

COMPARATIVE ANALYSIS: VARIOUS STATISTICAL FISH MERCURY STANDARDIZATION METHODS

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Monitoring fish mercury spatiotemporal concentration trends is of great importance in terms of scientific research and regulatory design. A robust and reliable analysis of trends of fish mercury is not only evidence for identifying sites with elevated mercury but also crucial reference for proposing mercury mitigation strategies and developing fish consumption advisories. Unfortunately, effective analysis based on fish monitoring data is normally hindered by difficulties in distinguishing the true spatial and temporal trends from total variances in fish-mercury concentrations complexed due to heterogeneity in fish samples of diverse species and trophic levels. This problem occurs since collecting fish samples with consistent characteristics (e.g., fish species, size, and sex) over large regions or over long time is difficult. Furthermore, budgetary constraints lead to a shortage of well-designed continuous monitoring programs, which force scientists studying spatiotemporal trends of fish mercury concentrations to use composite monitoring database. Composite database commonly integrates data from different monitoring program with distinct research objectives and protocols (e.g., aiming at specific species, regions and using different fish-cut for analysis). Using a composite database would thus complicate the interpretation of long-term trends embedded within fish mercury monitoring data. Surprisingly, there has been minimal efforts to evaluate the relative performance of these methods systematically. This research aims to review and to evaluate the performance of several published and representative statistical standardization models/methods on fish mercury: ANCOVA, multivariate regression, mixed-effects regression, polynomial regression, partial least squares regression and biotic mercury partitioning index (BMPI). We employed several statistical techniques (e.g., Principle Component Analysis (PCA), MANOVA, etc.) and the concept of machine learning (i.e., cross validation) to test the accuracy and robustness of the targeted standardization methods. This research is important since any further analysis (e.g., economics valuations, policy analysis) based on monitoring data may reach spurious results and misleading conclusions if the true spatial and temporal trends of fish mercury are not properly elucidated. This study is striving to serve as a clear guide on how to choose the right model for further research involving fish mercury trend analysis.

MP-031

COMPARISON OF UNCERTAINTY CONTRIBUTIONS TO THE EXPANDED RELATIVE STANDARD UNCERTAINTY OF HYDRIDE GENERATION AND ETHYLATION METHODS FOR THE DETERMINATION OF METHYLMERCURY IN SEAWATER

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Measurement of low methylmercury concentrations (MeHg) in seawater represents a major analytical problem due to low natural concentrations. Reference analytical method (aqueous phase ethylation coupled with gas chromatography and cold vapor atomic fluorescence spectrometry, Eth-GC-CVAFS) is widely used for MeHg determinations. Derivatisation of mercury species by hydride generation (HG), coupled with cryogenic trapping (CT), gas chromatography (GC) and cold vapor atomic fluorescence spectrometry has an advantage due to lower detection limits. Following optimization of HG-CT-GC-CVAFS for MeHg determination in seawater, we calculated measurement uncertainty budget using GUM/Eurachem guidelines for both methods. Expanded relative combined standard uncertainty (Uex,r) at the 95% confidence interval is obtained by applying a coverage factor k=2. At the highest MeHg concentration level (>80 pg/L), middle (2030 pg/L) and the lowest (<10 pg/L), Uex,r has a value of 11.1%, 15.0% and 21.3% for hydride generation, and 15.8%, 18.2% and 19.3% for ethylation, respectively. The highest relative contribution (index) to the expanded relative standard uncertainty in HG is from sample repeatability which accounts for 46.6% of Uex,r at the lower concentration level and slightly lower value at the highest MeHg level (39.9%). Similar trend is also observed in ethylation method, but the contribution indexes are lower (29.936.4%). Contribution indexes of MeHg standard repeatability are increasing with increased MeHg concentration in both methods; however, this trend is directly proportional to Uex,r decrease. Relative standard uncertainties for recovery are about 1.4% and 5% at all MeHg concentration levels for hydride generation and ethylation, respectively. Higher values in ethylation method are due to unreproducible and lower recoveries in ethylation (average 79%) caused by several procedure steps and incomplete sample extraction. At the highest MeHg concentration level (>80 pg/L), recovery has the highest uncertainty index for ethylation method (37%). Sample areas have a big contribution to Uex,r at lower MeHg concentrations for hydride generation (24.3%) due to readability of small peaks which is a consequence of 35% lower sensitivity of this method. Sample volume has three-fold higher uncertainty contribution index in ethylation than in hydride generation. This uncertainty is caused by sample losses during phase separation, back-extraction of sample, incomplete sample transfer to measuring vial and to instrument. Other uncertainty sources do not represent a significant contribution to expanded relative standard uncertainty of both methods.

MP-032

FIT FOR PURPOSE ANALYTICAL PROCEDURES FOR DETERMINATION OF METHYL MERCURY IN MARINE ENVIRONMENT

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Mercury is a global pollutant released into the environment from both natural and anthropogenic sources. Various mercury species differ greatly in their bio-physico-chemical properties such as toxicity and rate of bioaccumulation by organisms. Therefore the analysis of samples only for total mercury is no longer completely acceptable and provides only partial information about their impact on human health and the environment. As a consequence, considerable progress has been made in the development of techniques, which are capable of quantifying various mercury species. Future regulations on MeHg will require the standardized procedures for quantitative determination of alkylmercury species, therefore there is a strong need for development of robust analytical procedures providing reliable data on both, total mercury and its chemical species in the complex marine matrices.

Among its multiple tasks, IAEA Environment Laboratories (IAEA EL) in Monaco acts as the analytical support center for IAEA Member States laboratories and is the pillar of the Quality Assurance program for determination of contaminants in the marine environment. Several recommended methods for mercury and MeHg, based on the application of different analytical techniques are set up. Development and validation of reliable and sensitive method based on gas chromatographic separation and pyrolysis-atomic fluorescence spectroscopy (GC-py-AFS) in a variety of marine matrices is described in the the present study.

Since reliable results are still mostly dependent on sample preparation, this study aims to evaluate the efficiency of different procedures, namely microwave-assisted extraction (MAE) with HCl, TMAH KOH, alkaline digestion with KOH and enzymatic hydrolysis with protease, for the extraction of MeHg in marine samples. Determination was accomplished by hyphenated GC-py-AFS. The full validation process following international guidelines is presented and described.

The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure that determination of methyl mercury in biota samples could be achieved with demonstrated traceability to a stated system of reference within less than 3 % expanded uncertainty (k=2).

Overall, the results obtained with the developed analytical procedures are reliable, with stated expanded uncertainty, demonstrated traceability and fully validated methods. Hence, the methods presented could be recommended for its implementation in IAEA Member States Laboratories.

MP-033

A FIT FOR PURPOSE ANALYTICAL METHOD FOR DETERMINATION OF LOW LEVEL MERCURY IN SEAWATER: AN EXTENDED VALIDATION STUDY

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With the eventual ratification of the Minamata Convention on Mercury, United Nations/IAEA Member States will be required to establish or strengthen environmental mercury monitoring efforts. Among its many tasks, the IAEA Marine Environment Studies Laboratories (IAEA-MESL) in Monaco acts as the analytical support center for IAEA Member States laboratories and is the pillar of the IAEA Quality Assurance program for determination of contaminants in the marine environment. As such, IAEA-MESL has developed and validated a method for ultra-low level analysis of total mercury (THg) in seawater in order to better assist Member States laboratories with mercury analysis and mercury data quality assurance.

An analytical procedure using cold-vapor atomic fluorescence spectrophotometry (CVAFS) along with improved cleaning and sample processing methods was optimized and validated according to the recommendations of ISO-17025 standard and Eurachem guidelines. Importantly, a limit of detection and limit of quantification, after extensive cleaning and careful sample preparation, was possible at ultra-low levels (LOD = 0.01 ng kg-1; LOQ = 0.04 ng kg-1) using a relatively small sample volume (25mL). However, these values were variable over time and highly dependent on clean analytical technique. Additional parameters such as recovery, working range, repeatability, intermediate precision and combined uncertainty (28%, k=2; ~ 0.2 ng kg-1 concentration levels) were also carefully estimated.

All sample preparation steps were carried out in a clean laboratory environment under clean hoods (Class 100).

The traceability of obtained measurement results was also demonstrated. Particular attention was paid to the correct definition of the measurand in this validation study. The mass fraction of mercury dissolved in seawater (~0.20 ng kg-1) and mercury associated with solid particles (~0.22 ng kg-1) was estimated for a coastal seawater sample (~0.43 ng kg-1) from the Mediterranean Sea and the respective mass balance provided.

As part of the method validation, sample preservation methods, sample preparation methods and stability of samples were also investigated. As was found in previous research, preservation of seawater samples with 0.1% (v/v) nitric acid was acceptable for short-duration (up to 1 month) holding times. In this instance, nitric acid proved effective for sample stability for both unfiltered and filtered sample processing at concentrations around 0.47 ng kg-1 and 0.20 ng kg-1, respectively.

Additional validation of the proposed analytical procedure was achieved by participation in an Inter-Laboratory Comparison (ILC) study. The results provided were in excellent agreement with the assigned values of the ILC.

MP-034

DEVICE FOR SYRINGE (INJECTION) MERCURY CALIBRATION IN PICOGRAM RANGE

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The simple portable device for calibration of mercury analyzers is offered. The device uses a known method introduction of microvolumes of saturated mercury vapors in analytical cell. The basis of the method - known concentration of mercury vapor in unit volume at a specific temperature and pressure. In the proposed device the glass conical flask with mercury installed in thermal insulation box with melting ice, and microvolumes of saturated vapors sampled at 0°C. The concentration of mercury vapor at 0°C is 2.205 ng/ml. The dosage of saturated mercury vapors was performed by conventional insulin syringes with volume of 1 ml. The minimum volume for these syringes is 0.1 ml, i.e. at 0°C and 760 mm Hg. 220 pg of Hg. Using gas-tight chromatographic syringes with volume of 0.05 ml and below it is possible to dose amounts of mercury since 10 pg. The closed 75 ml flask is completely saturated with mercury for 4 minutes. The effect of reduction of mercury concentration in flask at selection intervals more than 30 s is absent. For stable results it is necessary to carry out preliminary training of syringes and introduce amendments to the atmospheric pressure. The assessment of possible diffusive losses of mercury from a syringe needle during transfer of vapors to analyzer was made. Reproducibility of various volumes dosage does not exceed 2%. Requirements to carrying out of calibration in pg range are developed. Filled with ice device keeps the temperature not less than 8 hours. This simple and cheap method provides precise, accurate and reproduced calibration. The device can be used in field conditions.

MP-071

TRACEABLE METHOD FOR MERCURY TOTAL MASS MEASUREMENT EMITTED FOLLOWING COMPACT FLUORESCENCE LAMP BREAKAGE

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Mercury is widely used in compact fluorescent lamps. The demand for these lamps is rising due to CFLs energy efficiency. Increased use of CFLs raised concerns due to potential exposure to toxic mercury vapour when broken indoor. Moreover, inappropriate storage, handling and recycling causes environmental concerns. Fully traceable data on total mass of Hg released after CFL breakage and validated measurement methods is currently lacking.

Mercury was trapped (preconcentrated) under constant flow of Hg free gas (i.e. nitrogen, argon, air) by several absorbers including gold traps and activated carbon traps. The most frequently used method for pre-concentration of Hg is based on amalgamation of elemental Hg using gold (Au) traps, which is followed by thermal desorption of Hg at 600 C and detection by CV AAS or CV AFS. The method is suitable for lower masses of mercury (up to 1000 ng). The precision of measurements is less than 15 %. Memory effects and passivation of Au traps can lead to loss of mercury or reduction in the amalgamation efficiency. Au coated silica sand is mostly used as absorbing media, however other noble metals as Au-Pt can be used to pre-concentrate Hg. Instead of silica Al2O3 can be used as Al2O3 is more stable at high temperatures. Au and Au-Pt coated Al2O3 sand were also used during experiment, however further research is still needed.

For higher Hg levels (in range of ng and g) traps with activated carbon are widely used. Mercury adsorbed on carbon from traps is further analysed by pyrolysis and CV AAS, CV AFS, and mass spectrometry (MS). Neutron activation analysis (NAA) is also used as a reference method. Activated carbon traps impregnated by sulphur or chlorine were tested for trapping elemental mercury in ng and g levels.

The main goal of this work was to develop an easy, on-line, sensitive and traceable method for the determination of released Hg from broken CFL bulb. A procedure involving a gas tight Plexiglas box with bulb crushing system, heated gold amalgamation trap coupled to a CV AAS mercury analyser with Zeeman background correction was developed. Calibrations of the CVAAS detection were conducted using diluted NIST 3133 Hg standard solution where the mass fraction of mercury is certified and traceable. Certified reference materials were used to check performance of analytical methods used.

2c: Sources and cycling of mercury in terrestrial ecosystems

MP-035

ENVIRONMENTAL GEOCHEMISTRY AND BIOAVAILABILITY OF MERCURY IN VICINITY OF KARABASH CU SMELTER

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By present time have been published large amount of data on heavy metals (but not on mercury) in environment of regions subjected to pollution of mining and nonferrous metallurgy. Mercury is constantly exist in the ores and concentrates as well as in industrial emissions and releases. Unfortunately, mercury emission from smelters not controlled officially. Research carried out in test site around the Karabash copper smelter (Southern Ural). The objective of this study was to investigate mercury cycle as result of atmospheric emission: precipitations (dry and wet) – soil – lake (water and sediments) – fish. Mercury concentrations in atmospheric dust deposition and rainwaters has been assessed. The results showed that mercury in precipitation mainly was in particulate (>2 μm) phase in the form of poorly soluble compounds, likely sulfides. The mercury content of atmospheric dust in 5-7 times higher local soils background; rainwater concentrations rarely exceed 0.5 μg/L. The area continues to suffer of acid rains (pH 3.5-4.5). Mercury concentrations in soils within 5 km zone from smelter stack (n = 20) ranged from 0.17 to 12.0 mg/kg. The maximum acceptable concentration (2.1 mg/kg) was exceeded in 30% of soils. The upper layer of bottom sediments in Lake Serebry showed extremely high concentration of mercury (up to 19 mg/kg), as well as other heavy metals from smelter emission (Pb, Zn, Cd, Cu and As). The assessment of bioaccumulation of mercury in physiological systems of fishes in comparison with background lake is made. The territory of Karabash geochemical anomaly is the natural-technogenic test area, which makes it possible to study degradation and restoration of environment at a changing technogenic load. It is shown that accumulation of mercury in fish tissue prevents the high content of Se in water and sediments.

MP-036

EFFECT OF ORGANIC MATTER DECOMPOSITION, SULFUR, SOIL TYPE AND FOREST GROWTH ON HG RETENTION AND BINDING STRENGTH IN FOREST SOIL

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Soil is the largest terrestrial sink for Hg and soils of Northeast US are elevated in Hg compared to US as a whole. Soil Hg concentrations are highly correlated to C and the fate of Hg in soil will be influenced by changes in climate and land use because these processes affect the C cycle. Similarly, changes in organic matter quality should affect Hg soil concentrations, because, presumably, Hg binding will change as quality changes. In this regard organic S is of particular importance because of the known high affinity of organic S groups to bind Hg. In this study, we look at the effects of OM decomposition (measured by δ13C), S, land use practice and soil type (pH) on Hg retention in forest soil in Bartlett, NH, U.S.A. The forests studied are of three ages – 15, 45 and 120 years, and contain two soil types - Inceptisol and Spodosol; Spodosols being more strongly acidic than Inceptisol soils. We collected soil from 10 replicate sites and oven dried at 30 0C. The soil samples were analyzed for C, δ13C, S, Hg, and bulk density. Soils were also extracted using DI water and analyzed for dissolved organic carbon (DOC) and Hg concentration, and partition coefficients (Kd) were calculated. The multiple regression of Log10 (Hg/C) vs. δ13C, Log10 (S/C), soil pH and forest growth was significant (p-value<0.0001; R2=0.92) and the three variables were individually significant (p-value<0.0001). The δ13C explains 33%, S/C 23%, pH 34% and forest growth 3% of the total variance in Hg/C ratio. Multiple regression of Log10 Kd vs. δ13C, Log10 S, pH and forest growth was also significant (p-value<0.0001, R2=0.56). again the first three variables were individually significant (p-value<0.0001). Most variance is explained by Log10 S (27%), δ13C (18%) and pH (10%), These results demonstrate that Hg retention (Hg/C) and binding strength (Kd) are strongly associated with the degree of OM decomposition, S concentration and soil type (pH). We do not see a significant effect of forest growth on Hg retention. However, there is slight difference in Hg retention between the three-forest growths which contributes to the total Hg retention in soil.

MP-037

GRAIN-SIZE DEPENDENCE OF MERCURY SPECIATION IN RIVER SUSPENDED MATTER AND SOILS IN A MERCURY MINING AREA AT VARYING HYDROLOGICAL CONDITIONS

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Suspended matter (SM) plays an important role in the transport of mercury (Hg) in aquatic systems. Information about Hg-species in this material is crucial to understand risk potential especially for Hg methylation and bioavailability. In the Idrija Hg mine (Slovenia) cinnabar (α-HgS) was mined and processed for centuries. These activities caused contamination of the Idrijca river system by dumping of ore roasting residues and atmospheric Hg deposition to soils attributed to excessive Hg emissions from the roasting plant. Cinnabar is the dominant Hg-species in the coarse-grained sediments of the Idrijca river where Hg methylation is general low, whereas organically-bound Hg has caused intense Hg methylation in the Gulf of Trieste (GT), the final sink for Hg released from the Idrijca catchment. Hydrology of the Idrijca river is characterized by high discharge events during heavy rains and snowmelt, which transports large amounts of SM towards the GT. However, the dominant Hg-species transported in SM and their specific source under varying hydrological conditions is largely unknown, but crucial to predict future transport of bioavailable Hg forms from the mining area to the GT.

We analyzed Hg concentrations and Hg-species (Hg-thermo-desorption) in SM and different grain size fractions of soils from the Idrijca catchment to evaluate changes in solid phase Hg-species under low and high flow conditions. Concentrations of dissolved Hg did not change significantly during low and high flow (median: 21.3 to 28.1 ng L^{-1}, respectively). Hg concentrations in SM in tributaries decreased with distance (~ 30 km) from the mine from 32.7 to 0.47 mg kg^{-1} related to Hg concentrations in fine particulate soil fractions (0.45-20 µm) which ranged from 56.2 to 0.53 mg kg^{-1}. Hg speciation in SM was dominated by organically-bound Hg forms at low flow (median: 95.5%) which decrease during high flow conditions (median: 53.8%) attributed to increased mobilization of cinnabar from riverbanks and mine residues. Our results show that aqueous Hg transport in the Idrija mining area is dominated by heavy rain events and mobilization of organically-bound Hg from soils indicating that the frequency of heavy rain events will control transport of bioavailable Hg to the marine environment.

MP-038

INFLUENCE OF AGRICULTURAL PRACTICES AND FLOODING EVENTS ON THE RELEASE AND BIOMETHYLATION OF MERCURY IN SOILS.

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The influence of temperature, redox conditions and organic matter on the release and biomethylation of mercury (Hg) is well documented but mechanistic processes in the terrestrial environment are ill-characterized although they might have a substantial impact on Hg behavior. This is particularly true for agricultural floodplain soils, where manure is commonly applied and also because climate predictions postulate an increase in temperatures and extreme weather events such as flooding. To study the effects of temperature, redox conditions and manure addition on the biogeochemical cycling of Hg, we chose a Hg-contaminated agricultural floodplain situated near Visp, Switzerland. There, between 1930 and 1976, an acetaldehyde-producing company released an estimated 50 t of Hg into a canal. During this period, the canal was cleaned multiple times and the Hg-rich sediments were distributed throughout the agricultural fields and private gardens, contaminating the whole valley. We studied three agricultural soils situated near the canal. The soils were incubated in triplicate microcosms under flooded conditions both with and without the addition of 2 wt.% organic matter (OM) for 11 days. Bulk soils were sampled before and after the incubation to test soil biomethylation while the soil pore water was sampled throughout the experiment to assess the presence of dissolved MeHg and the release of Hg. MeHg was extracted from soils with an optimized three-step selective extraction using 35% HCl, dichloromethane and L-cysteine. Hg species were measured with HPLC-ICP-MS, while total Hg and a range of relevant elements (e.g. Fe, Mn) were measured by ICP-MS. Further soil properties potentially affecting biomethylation and release of Hg were also measured (e.g. DOC, Eh and pH). Under these conditions, Hg concentrations in the pore water increased to over 40 µg/L within a few days, with a higher release in the manure-amended microcosms. Increasing Hg concentrations were correlated with those of Mn in pore water, suggesting a reductive dissolution of Mn (oxy-)hydroxides. The Hg release was followed by a subsequent decrease within two days. Interestingly, an increase in MeHg concentration was measured in the soils during the incubation (up to 28 µg/kg) while no MeHg could be detected in the pore water. Ongoing investigations include incubation experiments to determine more precisely the biomethylation mechanism and the decrease of dissolved Hg in pore water. This work is important in order to understand the influence of climate change and agricultural practices on the biomethylation and the release of Hg in the terrestrial environment.

MP-039

DISTRIBUTION OF MERCURY IN SLOVENIAN SOIL ACCORDING TO HIGH, MEDIUM AND LOW SAMPLE DENSITY SURVEYS

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Regional geochemical survey was conducted in whole territory of Slovenia (20273 km2). High, medium and low sample density surveys were compared. High sample density represented the regional geochemical data set supplemented by local high-density sampling data (irregular grid, n=2835). Medium-density soil sampling was performed in a 5 x 5 km grid (n=817) and low-density geochemical survey was conducted in a sampling grid 25 x 25 km (n=54). Mercury distribution in Slovenian soils was determined with models of mercury distribution in soil using all three data sets. A distinct Hg anomaly in western part of Slovenia is evident on all three models. It is a consequence of 500-years of mining and ore processing in the second largest mercury mine in the world, the Idrija mine. The determined mercury concentrations revealed an important difference between the western and the eastern parts of the country. For the medium scale geochemical mapping is the median value (0.151 mg /kg) for western Slovenia almost 2-fold higher than the median value (0.083 mg/kg) in eastern Slovenia. Besides the Hg median for the western part of Slovenia exceeds the Hg median for European soil by a factor of 4.

Comparing these sample density surveys, it was shown that high sampling density allows the identification and characterization of anthropogenic influences on a local scale, while medium- and low-density sampling reveal general trends in the mercury spatial distribution, but are not appropriate for identifying local contamination in industrial regions and urban areas. The resolution of the pattern generated is the best when the high-density survey on a regional scale is supplemented with the geochemical data of the high-density surveys on a local scale.

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MP-040

GEOCHEMICAL CONTROLS ON METHYLMERCURY PRODUCTION IN SHALLOW ALLUVIAL GROUNDWATERS IN THE CEDAR RIVER FLOODPLAIN

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The Cedar River watershed (20,800 km2 at study location) comprises much of eastern Iowa where row crop agriculture is the dominant land use resulting in disturbances of hydrology and nutrient cycling. Climatic change has likely driven increases in baseflow and the frequency of flood events in the region. Within this context, we report on hydrogeochemical controls on methylmercury (MeHg) production within a savanna oak floodplain and terrace fen complex along the Cedar River, with emphasis on microtopography and groundwater-surface water interaction in controlling MeHg production.

Total Hg (THg) in the Cedar River averaged 8.4±1.2 ng/L, with a mean filterable THg of 1.1±0.55 ng/L and a mean filterable MeHg of 0.085±0.020 ng/L. Within the floodplain where groundwater-surface water exchange occurs, filterable MeHg was elevated compared to the Cedar River, averaging 0.14±0.16 ng/L in shallow alluvial groundwaters and 0.34±0.17 ng/L in wetland ponds. Wells in sandy ridges had lower TDS, were more oxic (higher dissolved oxygen, lower Fe(II) and dissolved Mn) and had lower filterable MeHg (median = 0.049 ng/L) than silty swales (median = 0.098 ng/L). Our findings point to the importance of microtopography in controlling groundwater flow paths, dominant terminal electron acceptor processes and Hg methylation in alluvial groundwaters. Across all wells and sampling events, dissolved Mn was the only variable significantly correlated with filterable MeHg ($r = 0.46$, $p = 0.01$). Wetland surface water MeHg was also significantly correlated with dissolved Mn ($r = 0.70$, $p = 0.01$), suggesting involvement of Mn-reducing bacteria in Hg methylation at our study location.

Within the terrace fen complex, a strong redox gradient across the terrace (oxic) to fen (anoxic) boundary was accompanied by increased filterable MeHg in groundwater (0.054±0.035 ng/L in upland terrace vs. 0.11±0.12 ng/L in fen). MeHg concentrations in fen peat reached 6 ng/g dry weight or nearly 5% of total Hg; low MeHg concentrations in peat groundwater are attributable to strong MeHg sorption to peat organic matter and/or iron sulfide minerals. Hg concentrations in the macroinvertebrate Gammarus were nearly twice as high in fen organisms compared to those dwelling near the terrace discharge (52 vs. 28 ng/g dry weight median Hg), and indicate potential for trophic transfer of Hg in this high value ecosystem. Overall, our results suggest that alluvial groundwaters may be important zones of Hg methylation in terrestrial ecosystems. Ongoing work aims to quantify the importance of flood events to Hg cycling within this system.

MP-041

RADIOMETRIC TRACERS OF ATMOSPHERIC HG DEPOSITION TO VEGETATION

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The radioisotopes beryllium-7 (7Be, half-life 54 days) and lead-210 (210Pb, half-life 22 years) are produced in the atmosphere, are globally distributed, and by virtue of their radioactive decay provide time information for a variety of earth system processes. Because the occurrence of 7Be, 210Pb and Hg in terrestrial systems derives from a shared atmospheric source, an understanding of their relative behaviors during deposition and interaction with vegetation may provide insights into Hg post-depositional fate. To investigate the deposition and interception of atmospherically derived elements we measured 7Be, 210Pb, total Hg (HgT) and other metals in tree leaves (Quercus rubra, Eastern red oak) over four years in annual time series. Depositional flux of 7Be, 210Pb and major and trace elements was also measured weekly for five years at a site co-located with leaf collections. In oak leaves the concentrations of 7Be, 210Pb, HgT, Al, stable Pb and certain transition metals all increased linearly with time through the growing season, and this trend continued through autumn and winter senescence; red oak retains some dead leaves in the canopy through the dormant season. After 1 year of atmospheric exposure HgT concentrations averaged 92 ±33 ng g-1 leaf dry weight (mean ±1SD, n=7). The 7Be:210Pb ratio of the leaves maintained a dynamic equilibrium with measured atmospheric deposition, but due to the short 7Be half-life this ratio is sensitive to seasonal changes in leaf interception efficiency. A monotonic increase in 210Pb, 7Be, total Pb and HgT leaf concentrations through the annual seasonal cycle indicates that a portion of the depositional flux of each metal becomes irreversibly bound to leaf matter. Litterfall is the primary source of Pb and Hg to underlying soils in vegetated terrestrial systems, and our observations thus suggests that 210Pb may provide a valuable tracer and chronometer of Hg fate during its deposition from the atmosphere and transfer to soil systems.

MP-042

WHAT CAUSES INCREASED MERCURY FLUX FROM WET SOILS?

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Mercury is a neurotoxin that has significant impact on human health. Mercury is commonly found in its divalent form in environmental soils; however it can be converted to elemental mercury (Hg0), which can move from the soil to the atmosphere. It has been found that the addition of water to a soil can result in an increase in Hg0 emissions. The mechanism by which water influences mercury flux from soil, however, remains unclear. In 2005, Gustin Stamenkovic proposed that water could lead to a redistribution of reducible mercury within the soil matrix thus facilitating subsequent reduction and emission. However, water appears to increase mercury reduction in soils in the absence of a third party mechanism of said reduction. We conducted a number of controlled laboratory experiments in which dry, sifted soil samples were placed under Teflon flux chambers, and purified water was then added in distinct events at timed intervals. Consistent with reported studies, an increase in Hg0 flux was seen with the addition of water, with larger volumes of water led to larger Hg0 fluxes up to a point. However, in our work when a soil sample was wet with a given volume of water, allowed to dry and then wet with the same volume of water and left in the dark in the dark, the second wetting led to a larger increase in Hg0 emissions than the first water addition this was consistent across multiple samples and multiple subsequent wettings. These preliminary results suggest that additional factors may be at play when soil is wet in addition to the redistribution of reducible mercury.

MP-043

USING MOSS AS BIOMONITOR TO DETECT ATMOSPHERIC SOURCES OF MERCURY

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Mercury is a global health concern because of its toxicity to the human brain. Coal fired plants and sewage sludge incinerators are anthropogenic sources of mercury emission to the environment. Ambient air monitoring of such sources is expensive; however, moss has been used as a passive bio-monitor for airborne mercury due to its ability to absorb ions from the atmosphere. The purpose of this research was to study potential sources of mercury in New Haven, Connecticut, and determine whether moss is sensitive enough to detect a relatively small point source of atmospheric mercury pollution in a non-pristine environment. We hypothesized that there would be a direct relationship between the distance of the moss to identified sources of mercury, and the concentration of mercury in the moss samples. Local sources and patterns of distribution were studied by placing 21 samples of moss in three transects around a sewage sludge incinerator in New Haven and exposing them to ambient conditions for three weeks in July of 2015 and 2016. After collection, samples were analyzed and the patterns of mercury accumulation in the samples were correlated with distance from local sources of the metal. In 2015, moss samples closest to the incinerator showed mercury concentrations from 0.03 to 0.04 ppm, while moss placed further away had mercury concentrations from 0.02 to 0.03 ppm. Although samples from 2016 are still undergoing analysis, preliminary data corroborates the 2015 findings. Our data suggests New Haven (small source, non-pristine environment), and that the sewage sludge incinerator is acting a s a mercury source in the area.

MP-044

ATMOSPHERIC MERCURY DEPOSITION TO FORESTS IN THE EASTERN USA

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Atmospheric mercury in litterfall is an important form of deposition to forests, which comprise 50 percent of the land cover in the eastern USA. Mercury (Hg) was measured in autumn litterfall samples during 2007 to 2014 at a total of 27 National Atmospheric Deposition Program (NADP) precipitation-Hg monitoring sites in deciduous and mixed deciduous-coniferous forests in 16 states in the eastern USA. These data comprise one of the broadest and longest studies to date and captured the maximum litterfall-Hg concentrations and litterfall mass at the study sites each year, along with annual precipitation-Hg data. Rates of litterfall-Hg deposition were higher than or equal to precipitation-Hg deposition rates in 70 percent of the annual data, which indicates a substantial contribution from litterfall to total atmospheric-Hg deposition. Annual litterfall-Hg deposition rates from this study matched modeled dry-Hg deposition rates at NADP Hg-monitoring sites and may indicate the low end of the range of dry-Hg deposition to forests. Atmospheric-Hg deposition rates were statistically different among five forest-cover types in this study, and rates were highest in oak-hickory and maple-beech-birch types. Forest canopies apparently recorded changes in atmospheric-Hg concentrations over time because litterfall-Hg concentrations were significantly higher in 2007-2009 than in 2012-2014 and litterfall-Hg concentrations decreased year to year for all sites in the study periodfindings consistent with reported decreases in Hg emissions and atmospheric elemental Hg concentrations during this same time period. Methylmercury, the organic form of Hg which accumulates and concentrates in food webs, was detected in all litterfall samples at the study sites, documenting part of a terrestrial Hg cycle reported to affect wildlife such as songbirds and raptors and their prey. Findings from this study indicate that long-term measurements of Hg in litterfall and precipitation help to quantify most of the atmospheric-Hg deposition to deciduous and mixed deciduous-coniferous forests in the eastern USA.

MP-045

IMPACT OF ROOT SPIKES AND AIR HG EXPOSURES ON FOLIAGE, BARK, AND TREE RINGS OF AUSTRIAN PINES

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The relative importance of root exposure versus air exposure for plant uptake of oxidized mercury compounds has not been investigated extensively in controlled experiments. This project was a component of a larger one investigating the accuracy of tree rings as proxies for air exposures (i.e. atmospheric composition of Hg). This project involves the use of data collected from pines that were moved to different air exposures at 4, and 6-to-7 years old. In addition, tree cores were collected in multiple locations from trees >80 years old.

Here we discuss data collected using 4-year old Austrian pine trees grown from common genetic stock in Oregon that were exposed to three air treatments differing in GOM chemistry and GEM concentrations, and retained in the same soil. The trees were placed in: a greenhouse with GOM emitted from mining material (Hg-sulfur compounds), a greenhouse with HgBr2 permeated into ambient air, and a greenhouse with ambient air. In addition, a subset of trees was spiked with HgBr2 concentrations in solution of 100 ng/L applied to the roots 2-times a week for 5 weeks prior to being placed in different settings to investigate the impact of a root exposure versus air exposure. Foliar Hg concentrations, after growing in the different settings, were greater than the control trees (trees sacrificed when initially received), and increased over the growing season (June-September) for all exposures. There was no significant effect of the spike on tree ring concentrations. In addition, all tree rings were consistently higher relative to the controls. These results indicate permeation throughout the whole young tree.

MP-046

LINKING MINE WASTEWATER DISCHARGE TO INCREASES IN METHYLMERCURY CONCENTRATIONS IN A SUB-ARCTIC FEN

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Mines in remote northern regions have limited options for handling their wastewater produced through industrial and processing activities due to geographic isolation, cost, and energy requirements. Wetlands have a recognized capacity to assimilate nutrients and particulate matter, and since they are often geographically ubiquitous in these regions, are thus are an appealing water polishing option. However, some wastewaters contain elevated concentrations of sulphate, which is known to stimulate methylmercury (MeHg) production in wetlands, and in particular peatlands. To evaluate the potential impact of wastewater discharge containing sulphate on net MeHg production in peatlands, we conducted a large-scale field experiment that added simulated wastewater (containing nutrients and ~35 ppm sulphate) to a 0.98 hectare fen in the James Bay Lowland. In the summers of 2014 and 2015, simulated wastewater was loaded to the peatland at ~40,000 L/day for ~45 days each year. Samples were taken throughout the experimental site from pools and porewater via wells and piezometers.

In 2016, the site water was sampled as in previous years, but no additions were made to evaluate the potential recovery from nutrient loading. Two reference peatlands were also sampled. In both 2014 and 2015, the fen showed a dramatic increase in MeHg concentrations (site average 1.53 ng/L vs. 0.075 ng/L for reference sites) concurrent with the addition of sulphate, and an accompanying site average increase in %MeHg from ~4.21% before loading to ~28.9% during additions and ~18.0% post additions. In 2016, MeHg, concentrations at the experimental site dropped significantly from the years with additions, but remained above the reference site (background) concentrations. In all years, there was no measurable increase in MeHg concentrations at the outflow of the peatland, despite the dramatic increases in MeHg concentrations seen in the porewaters. These results reveal the sensitivity of pristine northern peatlands to sulphate addition with respect to MeHg, however we also found that increases in production do not necessarily translate into increases in export, and that recovery after additions may be relatively rapid.

MP-047

EVALUATING THE IMPACT OF ADDITIONS OF SULPHATE ON NET METHYLMERCURY PRODUCTION IN PRISTINE SUB-ARCTIC PEATS

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Sulphate additions to peatlands are known to increase methylmercury (MeHg) concentrations over time but little information exists about the effects of different levels of sulphate loading on the magnitude in intact natural peats. In remote, northern higher latitude peatlands, atmospheric loading of sulphate is extremely low areas where sulphate is higher are some sites of groundwater-surface water interaction, or where there has been land use change such as extractive mining. Here we present results from a replicated laboratory column experiment designed to examine a) the impact of different sulphate loads on net MeHg production in pristine peats naturally low in sulphate, and b) the degree to which sulphate derived from crushed mine waste rock stimulated net MeHg production in these same peats. Glass chromatography columns (30cm long, 4.8cm wide) with Teflon fittings were packed with peat, under anaerobic conditions. For the first experiment, continuous additions of three different sulphate concentrations (1, 5, and 30 ppm, plus controls) into the columns to simulate/represent the addition of sulphate-rich groundwater or wastewater containing sulphate to peat. For the second experiment, sulphate was delivered to the peat column by passing pH adjusted distilled water through a column packed with milled waste rock to simulate the pulse of sulphate that might be delivered from mine tailings. All sulphate additions stimulated net MeHg production, however the highest MeHg concentrations were seen in the 5 and 30 ppm treatments (1.82 +/- 0.18 ng/L and 1.23 +/- 0.11 ng/L, respectively vs 0.242 +/- 0.03 ng/L for the control columns) with the 5 and 30 ppm treatments also showing a more lagged response (48-72 hours) than 1 ppm, which was <24 hours. Results suggest that even very modest additions of sulphate to these pristine peats would result in a significant increase in MeHg in pore waters and potential downstream effects requiring careful consideration of both water and waste rock management for sulphate.

MP-048

DYNAMICS AND BUDGET OF MERCURY IN A SUBTROPICAL FOREST IN SOUTHWESTERN CHINA

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Forests are considered as a pool of mercury (Hg) in the global mercury cycle, Hg pollutions have also attracted many attentions for decades in suburb of southwestern China with a rapid economic growth. Studies have pointed out that the forest Hg is from atmosphere, dynamics and budget of mercury in some remote forests are not comprehensive and this risk of Hg releasing probably occur with the increasing of Hg accumulating in forest. However, limited data were published about dynamics and budget of mercury in a suburb area. In this study, a subtropical forest (nearby an industrial city, Chongqing) in southwestern China was chosen to study dynamics and budget of mercury in the forest, aiming to: 1) investigate the Hg concentration in various forest layers and analyze the dynamics of Hg in this forest; 2) understand the characteristics of Hg migration; 3) calculate the budget of Hg in this system. The results showed that the volume-weighted mean concentrations (VWM) and Hg fluxes of total Hg (THg) in precipitation, throughfall and runoff were 14.68 ± 6.13 ng·L-1, 31.64 ± 15.04 ng·L-1and 4.86 ± 0.31 ng·L-1, respectively and 16.51 μg·m-2·yr-1, 29.92 μg·m-2·yr-1, 1.29 μg·m-2·yr-1, respectively, which were higher than remote forests. Seasonal variations were also observed with peak THg value in winter and highest MeHg concentration in summer. Hg evaporation from soil/air interface (62.49 μg·m-2·yr-1) was the dominant pathway for Hg release from forest. The main pathway for Hg input into forest was litterfall (42 μg·m-2·yr-1), followed by throughfall and precipitation. The storage of Hg in forest field (including forest floor and soil profiles) was 130.37 mg·m-2·yr-1, which was much larger than input, this implied that the forest field was a big receiver for Hg. In this study, the Hg source was mainly from atmosphere in this forest system, and the Hg VWM in runoff has no risk for drinking water, but with the increasing accumulation of Hg in soil, this risk may be emerged.

MP-049

OBSERVATION AND ANALYSIS OF TOTAL GASEOUS MERCURY IN NAM CO STATION (4730 M A.S.L), A HIGHLAND BACKGROUND SITE IN THE INLAND TIBETAN PLATEAU

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A field campaign was conducted from 2 November 2014 to 22 March 2015 at Nam Co (Tibet, China) using a set of automatic atmospheric mercury speciation analyzers (Tekran 2537B with 1130 and 1135 units) for the measurements of Gaseous Elemental Mercury (GEM), Reactive Gaseous Mercury (RGM) and Particle-bound mercury (HgP). This study is one of attempts to present the valuable data sets of continuous measurements of atmospheric mercury species in the inland of the TP (Tibetan Plateau). Average concentrations of GEM, HgP and RGM were 0.94±0.19 ng m-3, 50.61±26.74 pg m-3 and 3.15±2.79 pg m-3 (mean±SD), respectively. The range of GEM, HgP and RGM as: GEM: 0.39-1.66 ng m-3; HgP: 4.88-157.84 pg m-3 and RGM: 0.18-29.73 pg m-3. For daily variation, GEM and RGM were relatively stable during monitoring, and HgP concentrations were much higher in wintertime than in later autumn and early spring. For details in diurnal variations of the mercury species, maximum GEM concentration was measured normally after sunrise whereas HgP reached its maximum before sunrise and RGM was maximum in the afternoon. Both convention and photochemical production were responsible for diurnal cycle of atmospheric mercury. Modeling results were relatively similar from potential source contribution function (PSCF) and concentration weighted trajectory (CWT) and results indicated that Nam Co Station was mainly affected by the air mass from South Asia. Western and central Nepal, central and east Pakistan and northern India were considered as potential source of Nam Co.

MP-050

A SIMULATION STUDY OF MERCURY EMISSIONS FROM THREE TYPES OF SOILS

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It is widely accepted that the amount of nature mercury emission is much larger than that of anthropogenic mercury emission. Multiple soil and meteorological parameters have been suggested to influence mercury release from soils. However, the relationships between the parameters and mercury release are still not very clear. In this study, we conducted a series of simulation experiments in lab to explore the effects of soil temperature and solar radiation on emission of mercury from soil. Field measurements were also conducted to verify the results. Three types of soil were collected in China including brown earth, black soil and red earth. The mercury concentrations in the three soils were 25.1 ± 0.4, 73.8 ± 2.1, 75.7 ± 2.4 ng/g, respectively, which are close to the background values of Chinese soils. Different gradients of solar radiation and soil temperature were designed in the orthogonal experiment. In addition, the concentrations of soil organic matter and other soil properties were examined, in order to investigate their influences. There are significantly logarithmic linear positive correlation between mercury emission and solar radiation, and significantly positive correlation between mercury emission and soil temperature. The minimum mercury emission flux (0.2, 0.6, 0.8 ng/m3/h) was observed under the dark condition and the maximum (2.1, 4.8, 6.3 ng/m3/h) was observed under the highest radiation intensity. The results showed that solar radiation is the primary driver for mercury emission from soil, which is the same as previous studies. Mercury emission flux in dark condition is about 5% - 15% of the flux in light condition and the percentage increases significantly as the soil temperature increasing. The flux in dark condition could be explained by thermal reduction of reactive mercury. Soil samples with similar mercury concentrations could have a difference of ~ 30% in mercury emission flux under the same experiment condition. The difference might be caused by the variation of soil organic matter and other soil properties.

MP-051

MERCURY AND METHYLMERCURY RELEASE FROM DOMESTIC SEWAGE TO THE ENVIRONMENT: SOURCE, DISTRIBUTION, SINK AND MASS FLOW FROM 2000 TO 2014 IN CHINA

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Based on the measurement of domestic sewage samples from 59 sewage treatment plants in China, we built the mass flows of total mercury (THg) and methylmercury (MeHg) release from this sector to the environment. As an important anthropogenic source which was frequently neglected before, THg and MeHg release from domestic sewage increased rapidly due to the population increase and economic development in China. There were 160 (-17% to 24% of overall

uncertainties) tons of THg and 260 (-17% to 25%) kg of MeHg released to the environment in 2014. Both THg and MeHg released to the aquatic environment decreased from 2000 to 2014, since the improvement of treatment rate in this period. THg and MeHg release to the pedosphere, such as land application and dumping of sludge produced by the sewage treatment plants, increased rapidly and threatened the local residents. THg emission from the disposition of sludge might be a neglected atmospheric source in China. The study on the release of THg and MeHg from urban areas to the environment by domestic sewage can fill the vacancy of anthropogenic source inventory, and could help identify feasible management measures in China.

2f: Mercury methylation: microbial and geochemical constraints

MP-052

EXPLORATION OF THE PHYSIOLOGY OF DESULFOVIBRIO SP. ND132 Δ(HGCA HGCB) MUTANT BY WHOLE GENOME RANDOM TRANSPOSON MUTAGENESIS AND MASSIVELY PARALLEL SEQUENCING

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Methylmercury (MeHg) is a neurotoxin generated by a subset of anaerobic bacteria. The overall process of methylation has been intensely investigated but until recently little has been understood about the molecular mechanism. Two genes, hgcA and hgcB, encoding for a corrinoid protein and 2[4Fe-4S] ferrodoxin respectively, have been shown to be essential for production of MeHg. Deletions of these genes in the model methylating organism Desulfovibrio desulfuricans ND132, both single gene deletions and in combination, show complete ablation of MeHg production. Currently, no data implicate HgcA and HgcB as part of a mercury detoxification system and, thus, a putative native function for these proteins remains in question. A newly described protocol, rapid transposon liquid enrichment sequencing (TnLE-Seq), allows for the rapid generation of mutant transposon libraries in the wild-type and mutant strains. DNA from each mutant pool will be prepared for next generation sequencing to determine the location of transposition and abundance of each mutant recovered. Identifying genes differing in fitness levels between the two strains may lead to physiological functions that are altered in the mutant. To date, no data have been provided on the overall response of methylating bacteria to mercury. Utilizing TnLE-Seq, we will also stress both wild-type and double deletion strains in order to observe the global response of the cell to toxic mercury levels.

MP-053

CHANGING PATHWAYS OF MERCURY METHYLATION ALONG TROPHIC GRADIENTS IN NORTHERN WETLANDS

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Methyl mercury (MeHg) can be produced by diverse microbes besides sulfate (SO42-) and iron-reducing bacteria, including syntrophs, methanogens, and fermenters. Many freshwater wetlands, especially those in high norther regions, are deficient in electron acceptors that support the traditional respiratory pathways of methylation. However, MeHg tends to accumulate to high levels in these wetlands. To investigate methylation pathways and to connect these with surface vegetation and microbial communities, experiments were conducted using peats from close to 50 sites in Alaska collected during the summers of 2014-2016. The sites were clustered using multiple factor analysis based on 1) pH and temperature; 2) CH4, CO2, and volatile fatty acids (VFA) production rates; 3) vascular plant composition, and; 4) non-vascular plant composition. pHs varied from <4 to >6. Mercury (Hg) methylation activity in laboratory incubations was determined using the short-lived radioisotope 197Hg(II) (½ life 2.67 days).

In the low pH Sphagnum dominated clusters, methylation rates were less than 0.1% day-1, while the high pH clusters dominated by Carex spp. and active methanogenesis, exhibited Hg methylation rates as high as 10% day-1. In intermediate sites, rich in Sphagnum with less Carex, a gradient in syntrophy and Hg methylation paths was observed. Molecular data revealed a gradient in methanogenic pathways, and an increased importance of fermentation as pH decreased. Incubation data also revealed a sequential loss in the use of specific VFA along the gradient from minerotrophy to ombrotrophy (pH decrease), signifying a gradient in syntrophy pathways. Hg methylation rates in conjunction with the use of microbial inhibitors and stimulators exhibited wide differences in effects along the trophic gradient, e.g., the methanogenic inhibitor BES lead to an inhibition of Hg methylation in minerotrophic sites, but stimulated methylation in intermediates sites, whereas inhibitors had no effect in highly ombrotrophic bogs.

Methanogens were the primary methylators in minerotrophic sites, whereas syntrophs were important methylators in intermediate sites. However, the type of syntrophy responsible for methylation likely varied along the trophic gradient. Primary fermenters were responsible for methylation in the most ombrotrophic sites. As high latitudes warm and decomposition rates and vegetation cover evolve, pathways of Hg methylation should change greatly with an increase in the role of respiratory processes like methanogenesis and probably SO42- and iron reduction, and a decrease in Hg methylation by primary and secondary fermenters (syntrophs).

MP-054

BIOLOGICAL MERCURY METHYLATION IN A CHRONOSEQUENCE OF WETLANDS: WHAT METHYLATORS DOMINATE THE METHYLATION ACROSS THE AGE GRADIENT?

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Earlier pure cultures studies showed that MeHg formation is mainly performed by microorganisms that metabolically rely on anaerobic respiration of sulfate and iron. Additionally, methylating SRB can still methylate Hg in the absence of sulfate via either fermentative growth or syntrophic interactions with methanogens. Yet, the role of syntrophy or fermentation in methylation has not been thoroughly examined in environmental samples. We made use of a unique natural geochemical gradient in a chronosequence of wetlands, where the young mires are more nutrient rich with circumneutral pH and feature an abundance of electron acceptors such as sulfate, while older mires hold much less nutrients, sulfate is scarce and pH is lower. Samples collected from three of these wetlands, representing a gradient in ages, were used for microcosm incubation experiments with specific metabolic resources, inhibitors and Hg isotope tracers. The experimental incubations were used to test the hypothesis that the pathway of Hg methylation varies as a function of wetland age and trophic status. The expectation would be that syntrophy dominates in old and intermediate wetlands, while respiratory pathway is more prominent in young, more nutrient-rich mires. The Hg methylation/demethylation rate constants (Km and Kd) were determined and by means of genomic analyses of incubated samples, microbial populations hosting and expressing the hgcA gene involved in the formation of MeHg could be determined. This was used to establish a relationship between the capacity for net Hg methylation and microbial community composition, with the aim to revealing the pathways of MeHg formation in the three wetlands. Our incubation results showed that microorganisms in young mires had the highest activity because of the highest CO2 and CH4 productions, then followed by intermediate and old ones. The addition of molybdate which is a specific inhibitor of SRB, and sulfate both inhibited CH4 productions but with a decrease and an increase in CO2 productions, respectively. The addition of volatile fatty acids (VFAs) such as lactate, propionate and butyrate, which are important substrates for syntrophic bacteria, enhanced the productions of CO2 and CH4. All of these findings may imply that syntrophic coupling of SRB and methanogens plays an important role on anaerobic respiration of organic matter in wetlands, subsequently impact the formation of MeHg.

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MP-055

MERCURY UPTAKE AND BIOAVAILABILITY IN A GRAM-POSITIVE FIRMICUTE, DESULFITOBACTERIUM METALLIREDUCENS

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The transport of inorganic Hg into the cell is a key step in the production of methylmercury in anaerobic organisms containing HgcAB. The ability to methylate is distributed across diverse phyla; however, intracellular uptake has only been studied in the δ-Proteobacteria and γ-Proteobacteria. In this study an iron-reducing firmicute, Desulfitobacterium metallireducens, was examined for intracellular Hg(II) transport to determine if the bioavailability and uptake of Hg(II) in this bacterium is similar to that observed in the proteobacteria. Washed cell suspensions of D. metallireducens accumulated Hg(II) when exposed to either Hg-cysteine or HgCl2 complexes, but did not support uptake in the presence of Hg-binding ligands such as sulfide, penicillamine, and glutathione relative to heat-killed controls. Uptake rates in the presence of Hg-cysteine complexes were linear for more than 4 hours; however, no methylmercury production was observed during the 20 h incubation. In contrast, similar experiments in the presence of Hg-cysteine with the Hg-methylating proteobacterium, Geobacter sulfurreducens, showed rapid Hg(II) uptake, methylation, and export of the newly produced methylmercury such that almost 100% of the added Hg(II) was methylated in ~4 h. These differences between these two iron-reducing strains are not due to changes in Hg-speciation, but rather due to enzymatic differences in the Hg methylating proteins, HgcAB, and/or other physiological differences in membrane structure, transporters, or the cytosol. Differences in the putative transporters responsible for Hg(II) uptake were observed between this firmicute and the proteobacteria. Unlike the proteobacteria studied (e.g. G. sulfurreducens), the protonophore, CCCP, failed to inhibit Hg(II) uptake in the firmicute, D. metallireducens. Furthermore, Zn(II) also had minimal or no effect on the cellular accumulation of Hg(II) when complexed to either chloride or cysteine. These specific results indicate that the model of active Hg(II) uptake through Zn transporters observed in proteobacteria may not be the primary mechanism of Hg(II) transport in D. metallireducens. Instead, Hg uptake in this firmicute appears to be a passive process likely mediated by facillitated diffusion through pores or channels in the membrane. These apparent differences in uptake and bioavailability of Hg(II) across phyla are critical to understanding the diverse microbial populations in the environment which are responsible for the production and accumulation of methylmercury.

MP-056

INSIGHTS INTO THE BIOMOLECULAR MECHANISM OF MICROBIAL MERCURY METHYLATION

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Mercury emissions as a result of silver mining, energy production and industrial use have led to a fourfold increase in mercury concentrations near the surface of oceans over the past 500 years. Bioaccumulation of highly toxic methylmercury (MeHg) in the food web is a significant public health concern. MeHg typically accounts for at least 90% of the mercury in fish. Inorganic mercury deposited in soils and sediments is transformed to MeHg by the metabolic activity of anaerobic bacteria and archaea. A two-gene cluster (hgcAB) is required for mercury methylation, and homologs of hgcA and hgcB have been identified in the genomes of more than 150 bacteria and archaea to date. The two genes are predicted to encode a corrinoid-dependent protein, HgcA, and a 2[4Fe-4S] ferredoxin, HgcB, consistent with roles as a methyl carrier and electron shuttle, respectively. However, the molecular structures of HgcA and HgcB and the specific mechanism of mercury methylation have not been determined. Furthermore, there is only limited knowledge about metabolic pathways linked to mercury methylation. This work aims to identify molecular interactions of HgcA and HgcB to elucidate the biochemistry of mercury methylation. Desulfovibrio desulfuricans ND132 strains were engineered for tandem affinity purification of HgcA and HgcB with 3xFLAG/TEV/StrepII tags in order to overcome limitations resulting from low abundance of the native proteins in cells. ND132 strains expressing tagged HgcA or HgcB retain mercury methylation activity at >50% of the wild-type strain. Tandem affinity purification, immunoblotting, crosslinking, and pull-down assays in combination with mass spectrometry are being used to identify other cellular proteins that interact with HgcA and HgcB. The results are expected to reveal protein-protein interactions, which will help delineate the roles of HgcA and HgcB in the context of microbial metabolism. Furthermore, identification of multiprotein complexes may enable molecular characterization that will provide insights into the mechanism of mercury methylation. A comprehensive understanding of the various geochemical and biochemical factors culminating in the production of MeHg will facilitate the development of effective strategies to reduce exposure to this pervasive neurotoxin.

MP-057

ABIOTIC AND BIOTIC PATHWAYS FOR DIMETHYLMERCURY PRODUCTION IN AQUATIC SYSTEMS

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The biogeochemistry of Hg in the oceans and the bioaccumulation of MMeHg in its food webs are of particular interest given that marine fish are the major source of exposure of people to MMeHg. A distinct characteristic of the Hg biogeochemical cycle in the ocean is the occurrence of dimethylmercury (DMeHg), a highly toxic and volatile form of Hg. Reported concentrations of DMeHg in marine waters range from 0.01-0.4 pM and DMeHg has been found to constitute up to 80% of the methylated Hg pool (MMeHg + DMeHg). The underlying formation pathways of DMeHg in the ocean however remains unknown. For the Arctic system, where a singifcant fraction of the methylated pool is present as DMeHg, incubation experiments have shown the methyation rate for the conversion of MMeHg to DMeHg to be one to two orders of mangitue higher than the methylation rate for inorganic Hg to DMeHg. Modelling work by Soerensen et al. futher suggest in situ formation of DMeHg in sea water from MMeHg, rather than from inorganic Hg. Suggested pathways of DMeHg formation from MMeHg under environmentally-relevant conditions include reaction of MMeHg with hydrogen sulfide, selenoaminoacids and methylcobalamin. Formation of DMeHg from MMeHg reacted with L-cysteine has also been suggested, however supporting experimental data is lacking. Up to 90% of the MMeHg in marine waters, and over 99% of the MMeHg in sediments and inside cells, is adsorbed to reduced sulfur groups on mineral surfaces or bound to thiol groups within organic matter. Thus, surface mediated processes leading to DMeHg production could be of great significance. Here, we experimentally show that the methylation of MMeHg to DMeHg can be mediated by different sulfide minerals, of different thermodynamic stability, as well as by organic dithiol compounds. We also show that the reaction can take place on mineral surfaces in either artificial sea water and/or when algal cell components are present, suggesting that MMeHg could be methylated intracellularly by iron-sulfur clusters on protein surfaces. We have also studied the formation of DMeHg from inorganic Hg and MMeHg in pure cultures of bacterial strains previously known to methylate inorganic Hg to MMeHg to examine bacterial production of DMeHg. We will contrast the importance of these various pathways based on our results and information about the potential for these reactions to occur in the marine environment.

MP-059

MICROBIAL METHYLATION OF MERCURY IN PADDY SOILS AND ITS MAJOR DRIVING FACTORS

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Mercury (Hg) has been considered to be a global pollutant because it can be transported over long distances. The Hg in environments could be microbially transformed into highly toxic methylmercury (MeHg), which would threaten human health and ecosystem safety. The MeHg in paddy soil is mainly from Hg microbial methylation, however, the underlying mechanisms of Hg methylation in the soil still remains poorly understood. This study is integrating chemical analysis and microbial ecology to explore the MeHg biosynthesis and characterize the community of Hg microbial methylators in paddy soils. Results show that MeHg concentration in soils was significantly correlated to Hg methylating gene (hgcA) abundance, which mainly distributed into sulfate-reducing microorganisms and iron-reducing microorganisms. In addition, geochemical factors such as soil contents of organic carbon, NH4+, SO42-, and Hg also influence the MeHg biosynthesis. Dynamics of MeHg formation and key microbial groups involved in Hg methylation will be monitored based on a series of mesocosm experiments, and the results will help to unravel the relative contribution of these Hg microbial methylators to MeHg production and the key geochemical factors influencing Hg methylation in the paddy soils. Finally, data from both field studies and incubation experiments will be incorporated to develop biogeochemical models for clarifying the microbial pathways and mechanisms of Hg methylation in paddy soils, which will be helpful to mitigate or manage soil MeHg pollution.

MP-060

USING MOLECULAR PROBES TO DETECT HGCAB FROM ENRICHED PERIPHYTON BIOFILM SAMPLES FROM THE EAST FORK POPLAR CREEK MERCURY CONTAMINATED SYSTEM

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Methylmercury (MeHg) is a harmful neurotoxin that bioaccumulates, thus posing risks to consumers and the environment. While a great deal of mercury (Hg) research has been conducted in aquatic environments, most work has taken place in lakes, reservoirs, and wetlands, with rivers and streams less well studied. The majority of research has also focused on macroscopic MeHg contributors like water and sediment as opposed to microscopic biofilms. Periphyton biofilms in the Hg contaminated East Fork Poplar Creek (EFPC) are a net source of MeHg in the system. Periphyton is a complex mixture of algae, microbes, and detritus that is attached to submerged surfaces in most aquatic ecosystems. These complex assemblages are ubiquitous throughout the creek and contain redox gradients that support Hg-methylating microbial activity even though the bulk water is well oxygenated. These biofilms include metal and sulfate-reducing Deltaproteobacteria and Firmicutes as well as methanogenic Archaea. Our initial attempt to utilize our hgcAB molecular probes on genomic DNA isolated from periphyton samples have been met with challenges. Direct analysis of periphyton was inconclusive, and likely due to the interference of abundant algal DNA in the gDNA extractions.

To increase PCR assay resolution and identify Hg-methylators, periphyton grown on silica disks deployed at upstream (closer to historic point of contamination) and downstream locations (~17km apart) of the EFPC were used to inoculate anaerobic enrichments. Three separate growth conditions for sulfate-reducing, Fe(III)-reducing, and methanogenic bacteria were established to promote growth of potential Hg-methylators and select against algae and other eukaryotes. PCR for hgcAB with gDNA isolated from these enrichments yielded conclusive evidence of hgcAB presence with a decrease in previously observed mispriming from untreated samples. Continuing studies will explore ways to process samples before extraction to better separate Bacterial and Archaeal organisms and DNA from eukaryotes. This accomplishment will allow for direct interrogation of the periphyton to identify Hg-methylators but also determine their native relative abundances. The latter is critical since the methylation extent and potential differs widely amongst Hg-methylating species.

Finally, the enrichments are being used to obtain site representative isolates from the EFPC which will be characterized and used to construct synthetic communities. This approach will allow for the observation of microbial interactions between Hg-methylators. Such interactions which may alter Hg-methylation and demethylation rates, extents, and potentials observed in single cultures, thus providing new and critical information to inform site management and restoration policies.

MP-061

THE EFFECT OF MARINE DISSOLVED ORGANIC MATTER ON THE FORMATION AND FATE OF Β-HGS NANOPARTICLES

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The methylation of mercury is known to depend on the chemical forms of mercury present in the environment and the bacterial methylating activity. In sulfidic sediments, under conditions of supersaturation with respect to metacinnabar, mercury precipitates as β-HgS(s) nanoparticles. Nano-sized particles have enhanced mobility, reactivity, and bioavailability relative to their micro-sized counterparts. Few studies have looked at the formation of β-HgS(s) nanoparticles precipitated in presence of marine DOM. In this work, we use dynamic light scattering (DLS), UV-Vis spectroscopy, and transmission electron microscopy (TEM) to investigate the formation and fate of β-HgS(s) nanoparticles (β-HgS(s) nano). They were formed from solutions containing inorganic mercury (HgII), dissolved sulfide, and marine DOM extracted from: Eastern Long Island Sound, Western Long Island Sound and at the shelf break of the North Atlantic Ocean, as well as with low molecular weight thiols. All the DOM used led to the formation of stable β-HgS(s)nano however, DOM extracted from the shelf break was less effective at inhibiting growth of β-HgS(s)nano relative to coastal DOM. In addition, multiple thiol groups on DOM likely cause inter-staple crosslinking of the β-HgS(s)nano leading to aggregation of particles, increasing their size as measured by DLS. Electron microscopy and calculations based on UV-Vis spectra confirmed that the β-HgS(s)nano however had similar radii, indicating that aggregation was occurring. We also showed that under anoxic conditions, β-HgS(s)nano can remain stable for weeks but will aggregate rapidly on exposure to air and light, suggesting limited persistence of the β-HgS(s)nano in surface waters. Furthermore, we showed that only at very high HgII:DOM ratios (>40 µmole/mg C), much higher than environmental levels, is the DOM concentration insufficient to effectively passivate the surface of β-HgS(s)nano. Our results also suggest that functional groups other than thiols could be involved in the passivation of β-HgS(s)nano by DOM. We will discuss the implications of the results from this work towards understanding the cycling of mercury and the presence of β-HgS(s)nano in sulfidic systems and, as β-HgS(s)nano are bioavailable to methylating bacteria, the implications to mercury methylation in natural ecosystems.

MP-062

DISTRIBUTION OF MERCURY-METHYLATING MICROBES ALONG SPATIAL AND TEMPORAL REDOX GRADIENTS IN A FRESHWATER LAKE

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Methylmercury (MeHg) is the bioaccumulative, neurotoxic form of mercury (Hg). It is taken up by algae and biomagnifies to dangerously high levels up the food chain. MeHg in freshwater lakes is either received from riverine runoff or is produced in situ from inorganic Hg(II) by anaerobic bacteria and archea that contain the hgcAB gene cluster. These microorganisms are tremendously diverse both metabolically and phylogenetically, and produce MeHg at different rates. In freshwater lakes, MeHg production can occur both in anoxic lake sediments and the anoxic water column, suggesting that these microorganisms inhabit both niches. In the water column of stratified lakes, changing redox conditions due to the onset of anoxia establishes a temporal and spatial gradient of electron acceptors and nutrients. The impact of these gradients on the distribution and identity of hgcAB-containing organisms, and thus on methylation potential, is not well understood.

Here, we examined the distribution of hgcAB-containing microorganisms relative to these gradients in water chemistry in a dimictic, eutrophic lake with high levels of MeHg. We collected depth-discrete DNA samples from Lake Mendota approximately every two weeks over the course of the summer, starting at the onset of anoxia and concluding at fall turnover. We also collected samples for water chemistry analysis to establish redox conditions and nutrient status at each of our sample sites. We performed PCR using primers for the hgcAB genes to determine which sites had organisms that contained hgcAB, then sequenced hgcAB amplicons from each of these sites for an overview of the diversity of hgcAB-containing organisms. Samples from representative sites were used to generate clone libraries for Sanger sequencing to further probe the diversity and to identify the organisms. These samples will be used for metagenomic sequencing to characterize the metabolic context for Hg methylation, as well as the community structure around methylation. Understanding how these varying conditions affect the identity of the methylating organisms will lead to a greater understanding of how MeHg production is influenced by the water chemistry of a lake, where and why methylation hotspots occur, and what role the methylating machinery plays in the physiology of methylating organisms.

MP-063

SORPTION OF MERCURY TO AGED IRON SULFIDES AND THE IMPLICATIONS FOR HG BIOAVAILABILITY

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The potential for inorganic mercury (Hg) to be converted to methylmercury depends on its bioavailability to microorganisms, which is in part controlled by the chemical speciation of Hg. In anaerobic settings, sulfides play an important role in controlling Hg speciation with numerous studies focusing on the formation of HgS and Hg-organic matter interactions and their effects on Hg bioavailability. Likewise, sulfide speciation can be dominated by ferrous iron sulfide (FeS), which can sorb or coprecipitate with Hg. The objective of this study was to determine if the aging state of FeS alters the reactivity and bioavailability of sorbed and coprecipitated Hg species. Synthesized FeS particles (with and without Hg) were aged under anaerobic conditions for multiple time frames spanning 1 hour to 1 month. Divalent Hg was subsequently sorbed to the non-Hg FeS for 1 day. The results indicated that more than 99% of the Hg sorbed to FeS (33 ug Hg per g FeS), regardless of the FeS aging state but in the Hg-Fe-S system aging affected Hg uptake (56% (1 hr) to 76% (1 month)). The recalcitrance of the Hg was assessed by exposing the particles to a solution of dissolved glutathione (a thiolate-based Hg chelator). In the sorbed Hg-FeS system, more Hg desorbed from the 1 month-old FeS than from the 1-h old FeS. For the Hg-Fe-S coprecipitate system, the desorption potential of Hg decreased with Hg-Fe-S aging time. Analysis of Hg speciation by X-ray absorption near edge spectroscopy (XANES) revealed qualitative differences between sorbed and coprecipitated Hg-FeS forms indicating a possible difference in binding mechanisms. However, the spectral quality was insufficient in elucidating quantitative information on the Hg phases present. In future work, these various forms of synthesized Hg-FeS will be exposed to cultures of methylating bacteria in order to compare bioavailability and Hg desorption potential from FeS particles.

MP-064

SOIL CHEMISTRY IMPACTS ON hgcAB DISTRIBUTION AND MERCURY METHYLATION RATES IN WETLAND SOILS

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The discovery of the genes responsible for microbial methylmercury production, *hgcA* and *hgcB*, has led to the identification of novel mercury (Hg) methylators with diverse metabolisms including iron and sulfate -reducing bacteria, syntrophs, and methanogens. Although these microorganisms are known to be widespread in nature, little is known about how soil chemistry shapes the distribution and abundance of Hg-methylating microorganisms. The objectives of this work were to 1) determine the abundance and distribution of *hgcAB*+ organisms in mid-Atlantic marshes and 2) to evaluate their distribution in relation to biogeochemical parameters in the marsh soils, including Hg methylation rates. The overall goal of this research is to assess the relative importance of site geochemistry and microbial community structure on Hg-methylation.

Soil cores were obtained from several marsh sites in the mid-Atlantic with salinities ranging from 2 to 13 parts per thousand. The sites were selected to contain different dominant vegetation types, including: no vegetation, *Typha latifolia and angustifolia*, *Phragmites australis*, and *Spartina patens*. The soil organic content varied from 1% to 73%, and porewater iron and sulfate concentrations varied according to both salinity and vegetation type. Microbial activity, as assessed by CO_2 and methane production, varied widely across sites, with methane production being highest in the lowest salinity marsh site and CO_2 production highest in the site dominated by *Spartina patens*. CO_2 production correlated with soil MeHg concentration, and methylation rates were highest in the low-salinity marsh samples. *hgcA* was found in all samples tested, and methylation rates correlated with *hgcA* copy number for deltas and methanogens for samples with a core depth of 0-4 cm. Work is ongoing to expand the data set for *hgcA* abundance across all the sample sites and core depths.

MP-065

IONIC STRENGTH CONTROLS ANAEROBIC HG UPTAKE

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In the absence of dissolved organic matter, chloride and sulphide are the dominant complexing agents affecting mercury (Hg) speciation in the environment. Bioreporters are good tools in evaluating bioavailable species of Hg. However, signal production for current Hg bioreporters requires oxygen, namely for lux and gfp gene encoded proteins, resulting in a paucity of data in anaerobic bioavailability of Hg species where it is methylated to toxic CH3Hg+. We developed and optimized a whole-cell Hg bioreporter using Escherichia coli 5 capable of functioning in aerobic and anaerobic conditions by transforming a vector containing the gene fusion between the regulatory circuitry of the mer-operon and a flavin mononucleotide-based fluorescent protein. The bioreporter exhibited no physiological limitations with respect to signal production over a chloride gradient ranging from 0 to 0.55 M. The bioreporter had a detection limit of 1 nM Hg(II) however we used 5nM Hg(II) as the optimal working concentration for Hg speciation assays. We report that HgCl4-2 is highly bioavailable under anoxic conditions in contrast to what was observed under oxic conditions where Hg was not bioavailable. HgCl3- was not bioavailable regardless of the presence of oxygen which we attributed to either coordination polymers consisting of [HgCl3-]x chains on the cell surface or molecular mimicry of HgCl4-2 onto anaerobically expressed periplasmic binding proteins specific for divalent polyatomic anions shuttling Hg to the inner membrane. The unexpected bioavailability of HgCl4-2 indicates the possibility of a novel mechanism for Hg uptake in marine environments.

MP-066

METHYLMERCURY FORMATION AND MOBILIZATION IN TROPICAL SOILS FROM A RAINFOREST WATERSHED (FRENCH GUIANA)

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Small scale gold-mining activities are both releasing anthropogenic amalgamated Hg and remobilizing endogenous Hg naturally accumulated in tropical forest soils. On the other hand, the main sources of methylmercury (MeHg) in tropical rainforest environments are still under debate. In this way, we investigated mercury (Hg) methylation pathways and microbial diversity in French Guiana rainforest soils from a small scale watershed containing significant concentration of endogenous Hg during early and late wet season (Febr June 2013). The experiments were realized along a typical soil gradient from upper oxisols down to hydromorphic soils. All these soils were strongly different in term of redox conditions, the hydromorphic soils being much more under reducing conditions, especially during the late wet season. Selected samples from different types of soils were investigated for potential methylation and demethylation rates during in situ experiments after incubations with isotopic tracers in the presence or absence of potential stimulators (sulfate, reducible iron or propionate). Soils and incubation batches bacterial communities diversity was characterized by NGS methods.

The microbial communities structure was extremely different between communities from upper oxisols, intermediate ultisols and hydromorphic soils periodically flooded with water. In most samples, community composition exhibit high proportions of Deltaproteobacteria dominated by syntrophic bacteria and Geobacteraceae, while Sulfate reducers were mostly found in reduced hydromorphic soils. Microbial diversity was compared with mercury transformation potentials (i.e. methylation and demethylation) in order to identify the main Hg methylators in tropical forest soils, especially taking into account sulfate reducers, iron reducers and syntrophs that were found at significant abundance. While the Hg methylation in oxisols remains negligible, significant methylation extent has been measured (up to ~1%.day-1) in hydromorphic soils during the late wet season. Such larger methylation extent was strongly enhanced by iron or sulfate amendment which suggests the main implication of both sulfate and iron reducing bacteria. The seasonal hydromorphic alteration in the lower section of the watershed (ie hydromorphic soils) provides geochemical and microbial conditions in soils favorable for in situ Hg methylation. During rain events, MeHg was also found to be actively remobilized into soil porewater and superficial flood stream. Tropical forest soils are thus able to generate significant amount of MeHg which can be further released to downstream hydrosystems, suggesting important implications for the environmental impact of Hg in such environments.

MP-067

ADSORPTION OF METHYLMERCURY ONTO GEOBACTER BEMIDIJENSIS BEM

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Anaerobic bacteria play an important role in the production and degradation of methylmercury (MeHg). The adsorption of MeHg onto anaerobic bacterial cells can affect the release of MeHg into aquatic environments as well as the uptake of MeHg for demethylation. The anaerobic bacterium Geobacter bemidijensis Bem has the unique ability to both produce and degrade methylmercury. To date, the binding of MeHg onto Hg-methylating and MeHg degrading bacteria remains poorly understood. In this study, we quantified the adsorption of MeHg onto G. bemidijensis Bem and applied X-ray absorption spectroscopy to elucidate the mechanism of MeHg binding on the bacterial cell wall. We hypothesized that MeHg adsorption on bacterial surfaces occurs via complexation with thiol functional groups in the cell wall. To test this hypothesis, fluorescent thiol-specific probes were used to determine the concentration of thiol functional groups on the bacterial surface. Methylmercury adsorption experiments were conducted over a range of MeHg concentrations and adsorption isotherms were used to quantify MeHg binding constants. The local coordination environment of methylmercury adsorbed onto G. bemidijensis Bem was then examined using extended X-ray absorption fine structure (EXAFS) spectroscopy. The results showed that MeHg adsorption onto G. bemidijensis Bem was rapid and equilibrium was reached in less than 1 hour. At low MeHg concentrations, up to 95% of MeHg was adsorbed to the bacterial cells. Blocking of the thiol functional groups with fluorescent thiol-specific probes significantly decreased the extent of MeHg binding. Results from the EXAFS analysis will be discussed in the presentation. Our study indicates that MeHg binds strongly onto G. bemidijensis Bem and that complexation reactions with cell wall thiol functional groups can affect the release and uptake of MeHg in anaerobic bacteria.

MP-068

EXPLORING ENVIRONMENTS FOR THE PRESENCE OF MICROBIAL MERCURY METHYLATORS USING HGCAB MOLECULAR PROBES

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The genes hgcA and hgcB have been shown to be responsible for microbial mercury (Hg) methylation. Recently, we developed a cost-effective PCR-based assay utilizing degenerate primers to assess the presence of hgcAB in genomic DNA (gDNA) from 30 pure cultures with the intention of application in the field. The goal for the present work was to survey environmental samples, including multiple soil/sediment/periphyton types from diverse geographical locations, for the detection and quantification of hgcAB from both known and novel microorganisms.

Here we present a selection of those environments which were examined, including; 1) sediment and periphyton collected from the Hg-contaminated East Fork Poplar Creek as well as the background Hinds Creek in Oak Ridge, Tennessee, each differing in relative methyl mercury (MeHg) and total mercury (HgT) concentrations, 2) sediment from microcosm experiments originating from these locations amended with carbon sources, 3) soil cores from the Marcell Experimental Forest in Minnesota, 4) organic carbon-rich permafrost cores from the Seward peninsula in Alaska, part of the Next-Generation Ecosystem Experiments (NGEE-Arctic), and 5) salt-marsh soils from the Smithsonian Environmental Research Center (SERC) on the shores of the Chesapeake Bay sub-estuary in Maryland. The hgcAB gene pair was present across all locations and the obtained PCR products amplified were observed at the expected size. Within each set of samples, hgcAB was only detected within the anaerobic zone. For each unique environment, gDNA isolation required optimization in order to account for differences in sediment texture, organic carbon content and pH, to name a few. Most importantly, our degenerate primers worked efficiently to amplify hgcAB and sequencing data revealed these genes were captured from uncultured and novel microorganisms among the samples as well as those known to be present at a particular location.

MP-069

EFFECTS OF NATURAL ORGANIC MATTER ON MICROBIAL METHYLATION OF MERCURY (HG) UNDER ANAEROBIC CONDITIONS

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Naturally dissolved organic matter (DOM) is known to affect mercury (Hg) redox reactions and microbial methylation in the environment. Several studies have shown that DOM may enhance Hg methylation, particularly under sulfidic conditions, whereas others found that DOM inhibits Hg methylation due to strong complexation between Hg and DOM molecules. In this study, we systematically investigated and compared the effects of DOM in Hg methylation by an iron-reducing bacterium Geobacter Sulfurreducens PCA and a sulfate-reducing bacterium Desulfovibrio desulfuricans ND132 under anaerobic conditions. The experiment was performed with washed cells in laboratory incubations in a phosphate buffered saline either in the presence or absence of a DOM isolate extracted from a mercury-contaminated creek water. Additionally, we compared DOM effects on Hg methylation in the presence or absence of 20 μM cysteine, which is known to enhance Hg methylation. Our results demonstrate that DOM effects on microbial methylation are bacterial strain-specific, time- and DOM-concentration dependent. Addition of DOM (at 0.1–5 mg/L DOC (dissolved organic carbon)) greatly inhibited Hg methylation by Geobacter Sulfurreducens PCA but somewhat enhanced methylation by Desulfovibrio desulfuricans ND132. However, addition of cysteine with DOM not only alleviated the inhibitory effects of DOM but enhanced Hg methylation by Geobacter Sulfurreducens PCA (at 0.1-2.5 mg/L DOC). These observations suggest that the effects of DOM and small thiol compounds such as cysteine on Hg methylation vary greatly, likely due to their influences on Hg bioavailability through complexation, and this effect should be considered when evaluating Hg methylation potential in the natural environment.

MP-070

CONTRASTING RESPONSES OF METHYLMERCURY ACCUMULATION IN RICE AND WHEAT TO BIOCHAR AMENDMENT

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There is growing concern about methylmercury (MeHg) accumulation in crops and thus enhanced dietary exposure to MeHg. Here, we explored the possibility of reducing grain MeHg levels by biochar amendment, and the underlying mechanisms. Two-year pot (i.e., rice-wheat-rice cultivation in biochar amended soils) and batch experiments (i.e., incubation of amended soils under laboratory conditions) were carried out, to investigate MeHg dynamics (i.e., MeHg production, partitioning and phytoavailability in soils, and MeHg uptake by rice or wheat) under biochar amendment (14% of soil mass). We demonstrate for the first time that biochar amendment could evidently increase net MeHg production in soils during rice (36-303% higher, compared to control) or wheat (52-292%) cultivation, probably explained by the release of dissolvable sulfate from biochar and thus enhanced microbial production of MeHg (e.g., by sulfate-reducing bacteria, indicated by copies of dsrAB genes). Interestingly, contrasting responses of MeHg accumulation in rice and wheat to biochar amendment were observed: biochar amendment resulted in reduced MeHg levels in rice (4992% lower, compared to control), but enhanced MeHg concentrations in wheat (48-84% higher). The differences were attributed to the changes in sulfur speciation in soils during rice (generally anoxic) or wheat (oxic) cultivation, examined by XANES, and thus different binding strength between MeHg and biochar amended soils. These observations together with mechanistic explanations improve understanding of MeHg dynamics in soil-plant systems, and support the possibility of reducing MeHg phytoaccumulation under biochar amendment.

2m: Monitoring regulatory effectiveness

MP-073

THE USE OF GEOMATICAL DATA IN THE DESERTIFICATION RISK'S CARTOGRAPHY-CASE OF SOUTH OF THE AURÈS REGION (ALGERIA).

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The risks cartography is a primordial step for the valuation and management of desertification phenomenon but it is a complicated spot, which necessitate a big amount of spatial and statistics data. The use of GIS permits to manage and use these data efficiency.

The objective of our study is the realization of the sensitivity to the desertification map of south of the Aurs region by means of Geographical information system in accordance with the MEDALUS method (Mediterranean Desertification and Land Use), which use the qualitative indices to define the sensitive environment zones to the desertification.

The creation of the database consist of four information layer (soil quality, vegetation quality, climate quality and the socioeconomic state) when the articulation in the space and in the time is submit to the validation on ground.

Once the database has corrected it help to the elaboration of the sensitivity to the desertification map with calculation of the indices of the sensitivity to the desertification (ISD).

MP-074

ENVIRONMENTAL MONITORING DURING THE U-864 COUNTER FILL INSTALLATION

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The wreck site of the World War II submarine U-864 is located at 160m depth near the island of Fedje on the west coast of Norway. The submarine carried 67 tons of metallic mercury. The sediment surrounding the wreck is heavily contaminated, and steel containers holding the cargo is still considered to be present inside the wreck. In 2015 it was decided to place a counter fill in front of the bow section which has been found to rest on a slope with unstable sediments. The Norwegian institute for water research (NIVA) was assigned to be responsible for implementation of the monitoring program required during the operations in May-June 2016, where objectives were to minimize spreading of mercury during installation of the counter fill material and to estimate the total amount of mercury transported out of the working area.

The counter fill covered a 200m by 60m area immediately north of the bow section of the wreck. Five landers measuring turbidity at 1,5m and 10m above sea floor surrounded the area. Data values were transmitted every five minutes through a connected buoy and Iridium satellite, presented visually on a website, and used to generate automatic alarms (when turbidity was >10 NTU). Alarms enforced water sampling from the designated Environmental Monitoring Vessel (EMV, Siddis Mariner), and the content of mercury was analyzed at the onboard laboratory within 30 minutes to a detection limit of 0.5 ng/L. Mercury levels above the threshold would trigger construction stop and mitigation actions. Daily routine sampling was done using hydrographic instruments for salinity, temperature, and turbidity (CTD) and LISST which measures particle size distribution. Analyses of mercury and grain size was performed on particles collected in sediment traps and vibrocore samples.

Mercury concentrations in the water samples never exceeded 1.3 ng/L, much less than the predetermined limit of 50 ng/l for initiation of mitigating actions. Operations were never stopped due to risk of mercury spreading. Estimated total flux of 34 g of mercury for the entire operation was two orders of magnitude less than the predetermined acceptance criterion of 3 kg. All the data collected through mercury analyses, CTD, LISST and the online monitoring provided information contributing to a more complete understanding of the mechanisms controlling the spreading of mercury during such operations. All relevant data consistently confirmed that the particle clouds observed was dust from the counter fill material with negligible contributions from resuspended sediments.

MP-075

TRENDS AND CURRENT STATUS OF MERCURY DEPOSITION IN NEW YORK STATE, USA

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Mercury (Hg), emitted through various fuel combustion, incineration, and industrial processes, primarily reaches sensitive ecosystems and built-up land via deposition. Since the 1990s, there have been numerous efforts to monitor Hg deposition in New York State, USA across a range of land uses and elevations. In this poster we summarize measurements of wet, dry, throughfall, and litterfall deposition across the state, including short-term intensive monitoring as well as long-term routine surveillance. Such measurements have provided a reference deposition baseline in New York, and continued monitoring will be needed to track emissions changes due to environmental policy at the Federal and regional levels.

MP-076

MONITORING TO EVALUATE TRENDS AND PATTERNS OF MERCURY CONCENTRATIONS IN PISCIVOROUS FISH OF NEW YORK STATE

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A spatial survey was conducted to examine the current status of mercury in fish in lakes across New York State, compare values with a previous survey conducted by New York State and identify trends in fish mercury concentrations that might be consistent with reductions in national emissions. In New York State alone, there are over 100 fish consumption advisories due to mercury contamination and elevated fish mercury concentrations remain a critical environmental issue. Human exposure to mercury largely occurs through the consumption of contaminated fish. The previous state wide survey completed in the early 2000s revealed high mercury concentrations in large piscivorous fish across the state, with the highest concentrations and most of the fish consumption advisories occurring in the Adirondack and Catskill regions. With recent decreases in U.S. mercury emissions, an effort to re-survey many of these lakes in New York State is nearing completion. This resurvey will focus on biophysical characteristics that were identified as important for mercury concentrations in the previous survey and to identify temporal trends and spatial patterns within New York state.

MP-078

AUTOMATIC SORBENT TRAP MONITORING SYSTEM - NEW NORMATIVE STANDARDS AND APPLICATION OF THIS COST EFFICIENT CONTINUOUS EMISSION MONITORING TECHNOLOGY

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Large Combustion Plants as e.g. coal and lignite fired power plants and cement kilns are worldwide one of the biggest mercury sources with emissions of more than 1.000 tons per year. As more and more countries sign the Minamata Convention there is an increasing request to reduce the mercury emissions of such plants. In the US were already published and were getting into force the US-regulations as e.g. the final National Emission Standards for Hazardous Air Pollutants (NESHAP) from the Portland Cement Manufacturing Industry the Mercury Air Toxic Standards (MATS) for combustion plants. Both rules have high demands on mercury emission control and continuous emission monitoring including very low emission limit values (ELVs) of approx. 1.5 µg/Nm³. In the European Union (EU) the revision of the BREF-document (Best Available Technology Reference document) for Large Combustion Plants is almost finished. The final document will be published in 2017. In the conclusions of the final draft is requested for e.g. coal fired power plants (with > 300 MWth) a continuous monitoring of the mercury emissions, with so called Annual Emission Levels (AELs) of 1 – 4 µg/Nm³.

In the US and also in the coming European regulations the continuous emission monitoring can be realized by Hg-CEMs or continuous sampling systems as Sorbent Trap Monitoring Systems (STMS). In the US the used sampling method is described in Performance Specification 12 B (PS 12B).In Europe will be published in 2017 a standard as CEN/TS, which describes the sampling method and the minimum requirements for the quality control.

This paper will give an overview of this coming CEN/TS. It will describe the method and the minimum and quality control requirements to assure reliable results. The paper will also show examples of flue gas conditions, under which the sampling method was modified to realize a possible sampling. Why and in which way such modifications can have influences on the measurement results are discussed in this paper. Additional it will show examples of realized applications on different industrial sites with the AMESA M STMS, including the description of the challenges which needed to be solved to realize successful monitoring.

MP-079

TRENDS IN MERCURY USE IN PRODUCTS: AN OVERVIEW OF MERCURY-ADDED PRODUCTS IN THE U.S. SINCE 2001

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Because mercury is a good conductor of electricity and has unique characteristics, it has been utilized in a wide variety of products, including barometers, thermometers and other measuring devices; switches and relays in commercial and industrial equipment; thermostats; button-cell batteries; dental amalgam; formulated products; energy-efficient light bulbs; and such novelty items as games and jewelry. Although overall use has declined in the U.S., mercury is still used in many applications, especially fluorescent and other lighting and dental amalgam. These mercury-added products are used in residential, commercial, as well as industrial environments.

Since 2001, the Interstate Mercury Education and Reduction Clearinghouse (IMERC) has collected information on mercury-added products sold in the U.S. This information is submitted by hundreds of manufacturers to satisfy notification requirements of the states of Connecticut, Louisiana, Maine, Massachusetts, New Hampshire, New York, Rhode Island, and Vermont. The notification reports are submitted every three years through IMERCs online system.

This poster shows mercury use in products every three years from 2001-2013, including data and graphs. IMERCs analysis of the 2016 data is not yet complete, but the poster does include general observations for the most recent information available at this time.

3b: Rice and other foods as sources of methylmercury exposure to humans

MP-080

PRODUCTION OF METHYLMERCURY IN HG(II) ION-ADDED FLOODED PADDY FIELD SOIL AND ITS ACCUMULATION IN RICE

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Recent studies have shown that rice is a significant source of dietary exposure to methylmercury (MeHg) for humans. The use of Hg in artisanal and small-scale gold mining (ASGM) has increased in many developing countries in rice-producing regions worldwide. The Hg released into rice paddy fields as a result of ASGM activity pollutes the paddy soil. Anaerobic soil bacteria in flooded rice paddy synthesize MeHg from Hg, leading to accumulation of MeHg in the rice plants. However, MeHg production from inorganic Hg in flooded paddy soil and its bioaccumulation in rice plants have not been extensively studied thus far. Here, we prepared different samples of Hg(II) ion-contaminated soils and cultivated rice therein, to confirm the differences in MeHg production in soils and its effect on MeHg accumulation in rice grain.

Pot experiments were performed in two different soil types—soil I and soil II, to each of which 10 mg/kg Hg(II) ion was added. Although the soils were well mixed under flooded condition, the vertical distribution of T-Hg concentration in these soils was not uniform, with higher concentrations in the upper layer and drastically reduced concentrations below. Rice was planted on June 12, 2015 and harvested on November 16. The flooded condition was maintained throughout the rice-growing season; the surface layer soil (about 3-cm thickness) and leaf and ear samples were collected every month. T-Hg and MeHg concentrations in these samples were measured using thermal decomposition-CV-AAS and HPLC-chemiluminescence method, respectively.

T-Hg and MeHg concentrations in the surface layer soil were monitored during the rice-growing season. MeHg production was confirmed in soil I after two weeks but in soil II after 3 months (October). The maximum MeHg concentration of soil I was 0.13 mg/kg in August and that of soil II was 0.11 mg/kg in October. MeHg concentrations in the flooded paddy soil showed wide variations. MeHg concentrations in the ear samples of brown rice from soil I and soil II were 0.52 ± 0.08 mg/kg (n=87) and 0.22 ± 0.03 mg/kg (n=96), respectively. MeHg and T-Hg concentrations were measured in all three parts of the brown rice grain—embryo, bran, and endosperm and found to be 3.18 and 3.86 mg/kg, 0.74 and 0.90 mg/kg, and 0.49 and 0.53 mg/kg, respectively. These results would be presented in detail in our subsequent study.

MP-081

QUANTIFYING THE HEALTH IMPACTS OF DIETARY FISH CONSUMPTION ADVISORIES FOR METHYLMERCURY AMONG INUIT IN LABRADOR

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Traditional diets of northern indigenous populations are rich in birds, fish and marine mammals, leading to high exposures to methylmercury (MeHg) and polychlorinated biphenyls (PCBs). Dietary advisories restricting consumption of local traditional foods are the predominant tool used to reduce risks associated with bioaccumulative contaminants. However, traditional foods contribute disproportionately to overall intakes of vitamin D, omega-3 fatty acids and other essential nutrients, and the transition to diets based on store-bought foods has been linked to adverse health outcomes including increased rates of obesity, cardiovascular disease and diabetes. Therefore, dietary advisories must weigh the risks posed by increased exposures to bioaccumulative contaminants against the risks posed by the loss of key nutrients, which act alternately on cardiovascular, neurodevelopmental and oncogenic endpoints. We quantify for the Inuit of Labrador, Canada the significance of local and store-bought foods to the overall dietary calories, MeHg, PCBs and a suite of nutrients. While local foods account for only 10% of total calories, they are the main source of MeHg (70%), PCBs (>90%) and a disproportionate source of omega-3 fatty acids (36%) and vitamin D (39%). We construct scenarios to forecast the cardiovascular, neurodevelopmental, cancer and nutritional impacts of substituting store-bought foods for local foods in comparison to the risks posed by increasing levels of MeHg. We find that substituting store-bought foods for local foods to preserve baseline MeHg exposures can reduce but not completely eliminate neurological impacts on developing children. However, the relative risk of cardiovascular death is greater for store-bought food substitution scenarios (population mean < 1.5) than the baseline diet for MeHg increases in local foods up to roughly seven times the baseline measured values. Food substitution scenarios generally increase population-wide cancer risks (population mean relative risk < 1.1, hepatic and colorectal cancers) relative to baseline and are associated with a decline in sufficiency of key nutrients (e.g., iron, phosphorus) of < 10% required daily intake. This work demonstrates that dietary advisories alone cannot be used to mitigate risks associated with increased exposures to MeHg and, in many cases, may increase these risks.

MP-082

SELENIUM-INDUCED REDUCTION IN METHYLMERCURY ACCUMULATION IN RICE: ANTAGONISTIC INTERACTION IN SOIL OR WITHIN PLANT

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Methylmercury (MeHg) accumulation in rice has great implications for human health. Here, effects of selenium (Se) on MeHg availability to rice are explored by growing rice under soil or foliar fertilization with Se. Results indicate that soil amendment with Se could reduce MeHg levels in soil and grain (maximally 73%). In contrast, foliar fertilization with Se (examining MeHg-Se interactions within plant) enhanced plant Se levels (312 folds) without affecting grain MeHg concentrations. These evidences, along with distinct distribution of MeHg and Se within plant, demonstrate for the first time that MeHg-Se antagonism in soil (i.e., reduced soil MeHg due to Se) rather than MeHg-Se interactions within plant might be the key process triggering the decreased grain MeHg levels under Se amendment. The observed MeHg-Se antagonism in soil could be mainly attributed to the formation of Hg-Se complexes (detected by TEM-EDX and XANES) and thus reduced microbial MeHg production. Moreover, selenite and selenate were equally effective in reducing soil MeHg concentrations, possibly because of rapid changes in

Se speciation. The dominant role of Se-induced reduction in soil MeHg levels, which has been largely underestimated previously, together with the possible mechanisms advance our mechanistic understanding about MeHg dynamics in soil-rice systems.

MP-084

MERCURY IN 15 DEEP SEA FISH SPECIES FROM THE NORTHEAST ATLANTIC AND FOOD SAFETY CONSIDERATION

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Previous studies have shown that tusk (Brosme brosme) is a species which seems to accumulate relatively high concentrations of mercury. Levels of mercury in tusk have exceeded the EUs maximum level for food safety in some fjord- and coastal areas. There has therefore been a need for a comprehensive survey of mercury levels in tusk caught in different geographical areas. There has also been a knowledge gap about the level of mercury in common ling (Molva molva) and other deep sea species caught in the same areas as tusk. During 2013-2016, 1396 tusk were sampled at 64 positions, distributed on fjord, coast and open sea areas from the Barents Sea in the north to the Skagerrak in the south and from Iceland in the west to Eastern Finnmark in the east. Additionally, 822 common ling were sampled from 41 positions, and 554 individuals of 15 different species were taken as bycatch. Fillets from each fish were analysed for a range of metals, including total mercury (Hg).

The results verified that mercury levels are relatively high in tusk fillet, with a total average of 0.34 mg/kg wet weight and mean concentrations above the maximum level of 0.5 mg/kg wet weight in fjords in western Norway, on the Skagerrak coast and in the Vestfjord area. Moreover, mean concentrations of 0.2 mg/kg wet weight and higher were found most places both along the coast and in open sea to the south of Lofoten. To the north of Lofoten levels were lower, and there was a general increase in mercury levels from north to south and from open sea to coast, and from the North Sea coast further into the fjords. Frequent consumption of tusk caught in many areas, particularly in the southern part of Norway, may thus contribute considerably to the tolerable weekly intake for mercury. For common ling and haddock a similar pattern was found for mercury levels, although concentrations were lower than in tusk. The order of species ranged by mercury concentration in fillet was this: Blackmouth catshark > ratfish > blue ling > tusk > hake > common ling > beaked redfish > rose fish > whiting = greater forkbeard = Atlantic wolffish > cod > haddock > spotted wolffish > northern wolffish.

MP-086

THE BIO-AVAILABILITY OF MERCURIC SULFIDE IN PADDY FIELD ECOSYSTEM

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Mercuric sulfide widely exists in the ore, sediment and soil of mercury mine area, which has a extremely low solubility in the nature. Its bio-availability is a focus of peoples concerning. In this study, rice was cultured in root boxes filled with paddy soil. mercuric sulfide with different polymorph and size were added, together with different species of sulfur-containing materials to investigate bio-availability of mercuric sulfide and its influence factors. ICP-MS, synchrotron radiation and molecular ecology methods were used for analyzing the content, distribution, speciation of sulfur and mercury in soil and rice samples. The results showed that the mercury content decreased from roots to stems and leaves then rice grains, and the main existence form was analogous to Hg(SG))2 in roots. With the increase of particle size of the mercuric sulfide, the content of mercury increased in brown rice. And different crystal type of mercuric sulfide was utilizated differently by rice, nano-metacinnabar was easier used than nano-cinnabar.

MP-087

MERCURY AND SELENIUM CONCENTRATIONS IN SEVERAL SPECIES OF COMMERCIAL SHRIMPS IN JAPAN

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Methylmercury (MeHg) is a neurotoxicant and people are mainly exposed to MeHg through the consumption of seafood. Selenium (Se) is known to antagonize the toxicity of mercury (Hg). Therefore, both MeHg concentration and Se/Hg ratio in seafood are important factors to consider the risk of seafood consumption. The muscles of 114 commercial shrimps representing 8 species from 10 countries were obtained at supermarkets in Kumamoto and Kagoshima prefecture. We determined the concentration of total mercury (T-Hg) and MeHg in the muscle of several species of commercial shrimp using heating vaporization AAS (simple analytical method: J. Toxicol. Sci. 41, 489-500, 2016), and Se concentration using ICP-MS. The median T-Hg and MeHg in muscle of black tiger shrimp from Australia were 62.1 ng/g and 58.6 ng/g wet weight (ww) and they were higher ($p<0.01$) than that of shrimp from Vietnam (8.5 ng/g ww: T-Hg; 8.2 ng/g ww: MeHg) and India (10.8 ng/g ww: T-Hg; 9.1 ng/g ww: MeHg). T-Hg and MeHg of vannamei shrimps from Ecuador were 31.1 ng/g ww and 30.6 ng/g ww, and they were higher ($p<0.01$) than that of shrimps from India (5.3 ng/g ww: T-Hg; 5.3 ng/g ww: MeHg) and Malaysia (11.2 ng/g ww: T-Hg; 11.0 ng/g ww: MeHg). T-Hg and MeHg of white shrimp from Bangladesh were 39.1 ng/g ww and 35.4 ng/g ww, and they were higher ($p<0.01$) than that of shrimps from Indonesia (16.0 ng/g ww: T-Hg; 14.6 ng/g ww: MeHg). The mean of MeHg/T-Hg ratios in all species of shrimps examined in this study were in the range of 90-99%. Median of Se concentrations (ng/g ww) in the muscle of shrimps from 3 countries were 322 (Vietnam), 343 (India) and 446 (Australia) for black tiger shrimp, 219 (India), 289 (Ecuador) and 305 (Malaysia) for vanammei shrimp, 391 (India), 412 (Bangladesh) and 385 (Indonesia) for white shrimp, respectively, indicating that Se levels in the muscle of these shrimps were similar compared to variation of Hg concentration. The results indicated that T-Hg and MeHg levels in the imported and domestic commercial shrimps in Japan were lower than the Japanese regulation levels of 300 ng/g ww for MeHg for fish, and the mean of Se/T-Hg molar ratios (16-106) were comparatively high. We can conclude that the shrimps examined in this survey will not pose particularly high risk concerning MeHg exposure.

MP-090

SCREENING OF HG LEVELS AND SPECIATION IN FISH SPECIES REPRESENTATIVE OF LOCAL CONSUMPTION FROM THE CHILEAN COAST

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Mercury pollution is considered a major environmental and public health concern. Considering its toxicity, Hg has been recently included in the top ten hazardous chemicals by the World Health Organization (1). Pregnant women and children in early life are considered the most vulnerable population to Hg harmfulness. In general, fish and seafood consumption is recognized as the most common pathway of Hg human exposure. It is especially troubling considering the recent and important increase of Hg in oceanic waters, recently reported (2).

Fishing is one of the most important industries in Chile and its commercial catch is the seventh-largest in the world. In Chile, the amount of mercury in marine species is regulated by the Food Health Regulations. It should not exceed 0.5 mg kg-1 for small fish species and for larger species, such as shark and albacore, the maximum limit is 1.5 mg kg-1 (3). However, the extent of coastal Hg levels and its concentration in fish is unknown. It is essential to establish a baseline contamination of MeHg in fish to further develop risk assessment actions in order to prevent Hg exposure via fish consumption and better inform environmental policy makers. The main aim of this work is determining the distribution and bioconcentrationof Hg in fish from the coasts of this South American country.

Representative fish species (such Merluccius gayi gayi and Genypterus chilensis) of local consumption were collected all over Chile's long coastline. Approximatively 0.1 g of muscle was digested and Hg content was determined by CV-AFS. Speciation was carried out by isotopic dilution GC -ICP-MS. The Hg content varies between 0.1 and 4.6 mg kg -1(dry weight). The highest Hg values correspond to Graus nigra, an endemic fish species. Regarding speciation, MeHg represents more than 95% of the total Hg content, irrespective of the fish species. The Hg levels associated to the different fish species and coastal regions will be discussed. The main perspective of this study is the elucidation of Hg potential sources and its fate in the marine systems by Hg stable isotopic characterization.

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MP-091

SELENIUM TO MERCURY MOLAR RATIOS IN WILD FISH SPECIES FROM NORTHEASTERN ATLANTIC OCEAN: INTER- AND INTRASPECIES VARIATION

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Seafood is the main dietary source of mercury (Hg) for humans and the trade-off between beneficial nutrients and undesirable elements is still a core for many studies. Selenium (Se) and Hg interaction in seafood is a particular example of this trade-off where their co-occurrence directly affect their bioavailability and toxicity. Since 50 years ago, protective effect of Se against Hg has been addressed, and within the last 10 years, Se:Hg molar ratio has received increased attention with regards to Hg risk evaluation , particularly for saltwater fish.

In this study, we examined the concentrations of Hg and Se and the Se:Hg molar ratios in 17 teleost fish species from Barents Sea, Norwegian Sea, North Sea, Skagerrak, North Atlantic and Norwegian fjords and coastal areas. The sampling area is limited to Svalbard Islands in the north, Yuzhny Island in the east, Strait of Dover in the south and west of Iceland in the west.

The mean Se levels ranged from 0.27 to 0.78 mgkg-1 in Atlantic cod (Gadus morhua) and wolffish (Anarhichas spp.) respectively. The mean Hg levels ranged from 0.04 to 0.77 mgkg-1 with the lowest level in Atlantic mackerel (Scomber scombrus) and the highest in blue ling (Molva dipterygia), and the mean Se:Hg molar ratios varied between 1.93 in blue ling and 43.18 in Atlantic mackerel with the major contribution of Hg levels. In general pelagic species had lower Hg levels and higher Se:Hg ratio and deep water demersal species had higher Hg levels and lower Se:Hg ratios. Most species had large portion (more than 50%) of specimens with Se:Hg ratio exceeding 5 except for tusk (Brosme brosme) (4% less than 1, 53% between 1 and 5) and blue ling (19% less than 1, 80% between 1 and 5).

In general, Hg concentration showed a gradually increasing trend from north to south and the rate of accumulation with increasing size also increased gradually towards the south. Se and Hg levels showed weak positive correlation (R-square from 0.15 to 0.47) except in mackerel, pollack, herring and saithe. Se:Hg ratios were negatively correlated to the fish length and the Hg levels. For all species, Se:Hg ratios were significantly different ($p < 0.05$) when individuals from different geographical areas were compared.

In conclusion, we can emphasize that fish from northeastern Atlantic Ocean are generally safe regarding Hg with few exceptions and Se may ameliorate the toxic effect of Hg to some extent.

MP-092

HIGH CONCENTRATIONS OF MERCURY IN YELLOWFIN TUNA (THUNNUS ALBACARES) FROM THE GALÁPAGOS MARINE RESERVE AND CONTINENTAL WATERS, ECUADOR

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Yellowfin tuna (*Thunnus albacares*) is one of the major large pelagic fish harvested in the Southeastern Tropical Pacific and also one of the most exported and traded. The tuna fishery is both industrial and artisanal in Ecuador, being the eighth country with most metric tons of tuna caught. This species is highly consumed by the coastal population in Ecuador and the Galápagos Island, an insular region part of Ecuador's territory. While the consumption of tuna fish is considered a source of nutrients that brings health benefits, tuna fish meat can also impose potential risks because of contamination by methylmercury. Methylmercury is a bioaccumulative and neurotoxic pollutant causing neurological and neurodevelopmental health effects in exposed people, mainly pregnant women and children, who may consume mercury-contaminated fish harvested from the sea. Very few studies have investigated mercury in large predatory fish in this equatorial region of the Pacific. The objective of this study was to assess the concentrations of total mercury (THg) in the red muscle of yellowfin tuna caught by artisanal fisheries in the Galápagos Marine Reserve and Ecuador's mainland coast. A total of 347 tuna were sampled (243 from the Galápagos and 104 from waters offshore Ecuador's coast). Muscle samples were analyzed using a DMA 80 mercury analyzer. 62.3 % of tuna samples exhibited size less than 70 cm. The mean concentration ± SD of mercury was 0.53 ± 0.55 µg/g (ppm) wet weight (ww). It was found that 8% of the tunas analyzed (n = 28) in this study were above the tolerable levels of Mercury established by FAO and the World Health Organization (1 ppm). The maximum concentration found was 6.8 (ppm) ww, being this one of the highest values of mercury reported for yellowfin tuna in the Pacific when compared to other studies. This study contributed with new baseline data on mercury concentrations in tuna from this region of the Pacific Ocean Basin and the initial information to establish tuna fish advisories with a limit of consumption of this species in both Ecuador and the Galapagos Islands with implications for public health in the long term.

MP-093

MERCURY RISK IN POULTRY IN THE WANSHAN MERCURY MINE, CHINA

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Rice, rather than fish, has recently been identified as the major exposure pathway of mercury (Hg) to inland populations of China. In recent years, in the Wanshan Mercury Mine (WMM), SW China, local crops were used more extensively to feed poultry and the awareness of Hg pollution in crops, led to a concern over Hg contamination in poultry. In this study, total mercury (THg) and methylmercury (MeHg) burdens in muscles (leg and breast), organs (intestine, heart, stomach, liver) and blood were investigated for chickens, ducks and geese in the WMM. Elevated THg and MeHg levels, especially in livers and blood, were observed in WMM poultry. The liver may serve as a filter of blood Hg, and may be a site of MeHg demethylation. Elevated THg and MeHg burdens were observed in chickens (THg: 15.3 to 238.1 µg; MeHg: 2.2 to 15.6 µg), ducks (THg: 15.3 to 238.1 µg; MeHg: 3.5 to 14.7 µg) and geese (THg: 83.8 to 93.4 µg; MeHg: 15.4 to 29.7 µg). Organs and blood constitute more than 50% of total burdens of THg and MeHg in poultry. This study demonstrated poultry can be a new important Hg exposure source for the WMM residents, and identified a high risk of Hg exposure for the local population.

MP-094

A NEW PATHWAY FOR METHYLMERCURY ACCUMULATION IN RICE PLANT: USING A STABLE ISOTOPE TRACER TECHNIQUE AND FIELD INVESTIGATION

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Methylmercury (MeHg) is a potent toxicant. Fish consumption is considered as the primary pathway of human MeHg exposure, and yet recent studies highlighted that rice is the main route of human MeHg exposure in inland areas polluted by mercury. Amounts of field investigations from mining and no-mining areas showed that rice plant, especially in grain has the highest ability for MeHg accumulation among crops. Where does this accumulation MeHg in rice plants come from, and how does it get there? So far, a consistent view think that MeHg in rice plant was originated from soil. In this study we hypothesized that air is another important pathway for MeHg accumulation in the rice plant. Stable isotope addition technique through field in-situ open top chambers(OTCs) experiments was performed to trace the uptake and translocation of gaseous organic mercury in rice plant and then quantify and assess the relative importance for assimilation of atmospheric organic Hg in rice plant. Firstly, we established a continuous low concentration DMe199Hg generation system based on the reaction of 2CH3-B12+Hg2++2H2O---(CH3)2Hg +2H2O-B12. Five levels of DMe199Hg in mixed air were set for OTCs experiments during rice growing stages. Me202Hg and Me199Hg concentration in rice tissues were determined by GC-ICPMS in rice tillering, jointing, heading, milk and mature stage. Results showed that total and tracer Me199Hg concentrations in rice tissues were statistical significance increase with the air DMe199Hg levels and the extension of growth period, which clearly reveal that rice can uptake DMeHg from air. Examining to the percentage of Me199Hg (tracer) in rice tissues to those in whole plant suggests that leaf and stem absorb large amounts of DMeHg during tillering and jointing stages, and then most of those translocated to ear of rice, and finally accumulated in the rice grain. The relative contribution percentages of tracer DMeHg to total MeHg in rice tissues calculated by model are increasing with the gaseous DMeHg concentration, and more than half of MeHg in rice leaves and about 40% to 90% of MeHg in rice grain are obtained from air with DMeHg concentrations from 16.0 to 1033.3 pg m-3. Furthermore, the preliminary investigations show that DMeHg concentration was 2 to 20 pg m-3 in surface air and 1-15pg L-1 in surface water at flooding paddy field in Wanshan mining areas, implying that the new pathway from air for MeHg accumulation in rice plant should be comprehensive evaluation at this mining areas.

MP-096

SULFUR MODULATES MERCURY TRANSFORMATION AND ACCUMULATION IN RICE PLANT GROWN IN MERCURY CONTAMINATED SOILS

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Sulfur (S) is an essential element for plants and its biogeochemical cycling is strongly linked to the species of heavy metals and their transformation in soils. In this work, the effects of S (elemental sulfur and sulfate) treatment on rice growth, Hg accumulation in rice, and Hg geochemical fractions in rice rhizosphere soil were investigated. It was found that both elemental sulfur and sulfate promoted the total Hg (T-Hg) and methylmercury (MeHg) accumulation in rice grains, stalkleaf, and root but did not affect the rice growth. Sequential extraction analysis of Hg geochemical fractions in rhizosphere soil displayed increased bioavailable Hg in paddy soils. The result was further proved with Hg L3-edge X-ray absorption near-edge structure (Hg L3-edge XANES), indicating that S treatment reactivated the non-bioavailable Hg in the rhizosphere soils. This finding is significant since it suggests that the application of S fertilizers in Hg contaminated farmland can increase the accumulation of both T-Hg and MeHg in crops, which may bring much serious health problems to people depending on them. It should raise cautiousness when using sulfur-containing agents in Hg contaminated soils. On the other hand, this study also suggests that S treatment could be an effective measure to mobilize the Hg that was hard to be absorbed by plants and to accelerate the phytoremediation efficiency in Hg contaminated soils.

MP-097

ELEVATED MERCURY BODY BURDEN IN PACIFIC SIDS WOMEN OF CHILDBEARING AGE

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There is little information about the body burden of mercury in Pacific Small Island Developing States (SIDS) populations, and consequently little understanding in this UN subregion about the potential adverse impacts on human health, development, intelligence and, by association, economic costs. What little data exists highlights the unusual phenomenon of high mercury levels in places where there is limited industrial pollution or coal-based power generation.

To advance the understanding of global mercury pollution impacts, IPEN undertook a study focussing on determining the methylmercury levels borne by women of childbearing age (18-44 years) in Pacific SIDS, on the basis that they represent a vulnerable sub-population. Methylmercury body burdens are particularly important for women contemplating pregnancy, because of the possible impacts of methylmercury on the developing foetus with regard to health and development endpoints.

The hypothesis for this study is that women from Pacific Islands have elevated mercury body burdens due to consumption of seafood. Members of IPENs global network coordinated with civil society partners to collect hair samples from female participants. In total, 239 hair samples from 7 Pacific SIDS were taken, analysed for mercury concentrations and compared against the 1 ppm level that approximately corresponds to the USA EPA reference dose. Preliminary results show highly-elevated mercury body burden for women in Pacific SIDS, with the most likely exposure pathway being seafood consumed as the principal dietary protein.

As methylmercury is considered an endocrine-disruptor, this may have some bearing on the rapid increase of non-communicable diseases (including diabetes and hypertension) that were deemed high priority in the outcome report from the 2014 Third International SIDS Conference.

Industrial and related sources of mercury pollution are negligible in the Pacific subregion, suggesting diffuse atmospheric mercury deposition to oceans is a key source of methylmercury contamination in seafood. While this sample size is relatively small, it illustrates a disturbing trend that may compel Pacific SIDS governments to request a broader, deeper study through the WHO. We conclude that greater efforts are needed to reduce atmospheric mercury emissions, in order to avoid contamination of fish and thus protect Pacific SIDS women and their unborn children countries from the adverse impacts of elevated methylmercury body burden.

3c: Risk assessment of mercury exposure to fish, birds, and wildlife

MP-098

AVIAN MERCURY EXPOSURE AND TOXICOLOGICAL RISK ACROSS WESTERN NORTH AMERICA: A SYNTHESIS

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Methylmercury contamination of the environment is an important issue globally and birds are useful bioindicators for mercury monitoring programs. We synthesized all of the available data on mercury contamination of birds in western North America. We obtained original data from multiple databases and conducted a literature review to obtain additional mercury concentrations. In total, we compiled 29,219 original bird mercury concentrations from 225 species, and obtained an additional 1,712 mean mercury concentrations, representing 19,998 individuals and 176 species, from 200 publications. To make mercury data comparable across bird tissues, we used published equations of tissue mercury correlations to convert all mercury concentrations into blood-equivalent mercury concentrations (µg/g wet weight [ww]). Blood-equivalent mercury concentrations differed among species, foraging guilds, habitat types, locations, and ecoregions. Piscivores and carnivores exhibited the greatest mercury concentrations, whereas herbivores and granivores exhibited the lowest mercury concentrations. Bird mercury concentrations were greatest in ocean and salt marsh habitats and lowest in terrestrial habitats. Bird mercury concentrations were above toxicity benchmarks in many areas throughout western North America, and multiple hotspots were identified. We also summarized the published toxicity benchmarks established for multiple tissues, and translated them into a common blood-equivalent mercury concentration. Bird health, physiology, behavior, and reproduction were affected across a range of blood-equivalent mercury concentrations, with many documented effects in the range of 1.0 to 3.0 µg/g ww and more severe effects occurring over 3.0 µg/g ww. Overall, 66% of birds sampled in western North American exceeded a blood-equivalent mercury concentration of 0.2 µg/g ww (above background levels), which is the lowest-observed effect level, 28% exceeded 1.0 µg/g ww (moderate risk), 8% exceeded 3.0 µg/g ww (high risk), and 4% exceeded 4.0 µg/g ww (severe risk). Mercury monitoring programs should sample bird tissues that are most-easily translated into tissues with well-developed toxicity benchmarks and that are directly relevant to bird reproduction. These high priority sampling tissues include whole blood, eggs, and juvenile down feathers. Our results indicate that mercury contamination of birds is prevalent in many areas throughout western North America, and large-scale ecological attributes are important factors influencing bird mercury concentrations.

MP-099

A CRITICAL EVALUATION OF THE UTILITY OF EGGSHELLS FOR ESTIMATING MERCURY CONCENTRATIONS IN AVIAN EGGS

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Eggshells are a potential tool for non-lethally sampling contaminant concentrations in bird eggs, yet few studies have examined their utility to represent mercury exposure. We assessed mercury concentrations in eggshell components for 23 bird species and determined whether they correlated with total mercury (THg) in egg contents. Additionally, we designed a multi-experiment analysis to examine how THg is partitioned into eggshell components, specifically the hardened eggshells, the material adhered to the eggshell, and the inner eggshell membrane. THg concentrations in eggshells were much lower than in egg contents, and almost all of the THg within the eggshell was contained within the material adhered to eggshells and the inner eggshell membrane, and specifically not within the calcium-rich hardened eggshells. Despite having very little mercury, THg concentrations in hardened eggshells had the strongest correlation with egg contents among all eggshell components. However, species with the same THg concentrations in eggshells had different THg concentrations in egg contents, indicating that there is no global predictive equation among species for the relationship between eggshell and egg content THg concentrations. Further, for all species, THg concentrations in eggshells decreased with relative embryo age. Although the majority of mercury in eggshells was contained within the inner membrane and material adhered to the eggshell, and not within the hardened eggshell, THg concentrations in hardened eggshells can be used to estimate THg concentrations in egg contents if embryo age and species are addressed.

MP-100

SEASON, MOLT, AND BODY SIZE INFLUENCE MERCURY CONCENTRATIONS IN AECHMOPHOROUS GREBES: IMPLICATIONS FOR ESTIMATING EXPOSURE RISK

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Mercury is highly toxic to fish and wildlife, and can impair behavior, physiology, survival, and reproduction. Sampling bird blood is a common means for evaluating site-specific exposure risk of mercury to wildlife. However, blood mercury concentrations can change rapidly through time, due to changing environmental factors at a site and changing physiological factors within the birds themselves. We studied seasonal and physiological influences on mercury concentrations in western grebes (Aechmophorus occidentalis) and Clark's grebes (A. occidentalis) across 29 lakes and reservoirs in California, USA. Additionally, at three of these lakes, we conducted a time series study, in which we repeatedly sampled grebe blood mercury concentrations during the spring, summer, and early fall. Grebe blood mercury concentrations were higher among males (0.61±0.12 µg/g ww) than females (0.52±0.10 µg/g ww), higher in Clark's grebes (0.58±0.12 µg/g ww) than western grebes (0.51±0.10 µg/g ww), and exhibited a strong seasonal pattern (decreasing by 60% from spring to fall). Further, the relationship between grebe blood mercury concentrations and wing primary feather molt exhibited a shallow U-shaped pattern, where mercury concentrations were highest among birds that had not yet begun molting, decreased approximately 24% between pre-molt and late molt, and rising approximately 19% from late molt to post-molt. Because grebes did not begin molting until mid-summer, lower grebe blood mercury concentrations observed in late summer and early fall were consistent with the onset of primary feather molt. However, because sampling date was a much stronger predictor of grebe mercury concentrations than molt, other seasonally changing environmental factors likely played a larger role than molt in the seasonal variation in grebe mercury concentrations. In the time series study, we found that seasonal trends in grebe mercury concentrations were not consistent among lakes, indicating that lake-specific variation in mercury dynamics influence the overall seasonal decline in grebe blood mercury concentrations. These results highlight the importance of accounting for sampling date, as well as ecological processes that may influence mercury concentrations, when developing monitoring programs to assess site-specific exposure risk of mercury to wildlife.

MP-101

SUBCELLULAR DISTRIBUTION OF MERCURY IN POLAR BEAR (URSUS MARITIMUS) LIVER

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Polar bears are long-lived marine mammals, which occupy apical trophic positions in Arctic food webs. Accordingly, they are exposed to high levels of dietary mercury (Hg), the majority of which is likely derived from anthropogenic sources. Despite high levels of exposure, recent data indicate that polar bears accumulate relatively low concentrations of total Hg in their brain stems (~0.07 ppm wet weight). Conversely, concentrations of total Hg of 30 ppm wet weight, mainly in the form of inorganic Hg, have been reported for polar bear liver tissues. The accumulation of high concentrations of inorganic Hg in the liver may be a result of demethylation of more toxic methylmercury (MeHg). MeHg demethylation in the liver is often considered a detoxification mechanism and may serve to protect the brain and explain the low total Hg concentrations observed therein. While it is well known that polar bears accumulate elevated inorganic Hg concentrations in liver, it is not well understood how inorganic and MeHg are distributed at the subcellular level. In this context, we measured total Hg and MeHg in the livers of 42 polar bears and explore how these forms of Hg are distributed at the subcellular level. We aim to better asses the risk of Hg exposure in polar bear by applying a subcellular partitioning procedure to separate a subset of livers into putative metal-sensitive fractions (cytosolic enzymes, organelles) and detoxified metal fractions (metallothionein-like proteins and peptides, granule-like structures). Mercury in metal-sensitive fractions has the potential to cause negative health effects. Polar bear livers were subjected to a subcellular partitioning procedure using differential centrifugation, NaOH digestion, and heat denaturation techniques. The resulting fractions were analyzed for total and MeHg by direct mercury analyzer and GC-CVAFS, respectively. Results of this research indicate that inorganic Hg is the predominant form of Hg in polar bear livers (mean = 99%) over a wide range of total Hg concentrations (3.5 to 32 ppm wet weight). The subcellular distributions of non-essential metals, such as Hg, may provide important insight into detoxification/toxicity mechanisms at the subcellular level, and may ultimately allow for better risk assessments.

MP-102

INFLUENCE OF A DAM ON THE MERCURY CONTAMINATION OF FISH IN FRENCH GUIANA SINNAMARY RIVER

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The Petit-Saut hydroelectric dam was filled in 1994 on the Sinnamary River in French Guiana (Amazonian basin). Since dams construction physicochemical conditions were monitored in the reservoir and in the river downstream to characterize the impact of rain forest flooding and role of hydroelectric reservoir on mercury methylation. Indeed, French Guiana soils contain high level of mercury coming from atmospheric depositions and also from illegal goldmining sites that use elemental mercury for gold extraction.

Previous studies that analyzed monitoring results showed that physicochemical modifications generated by dam construction led to an important production of methylmercury (MeHg) in the anoxic part of the reservoir and in the downstream river.

Sampling was carried out over 22 years and 5500 fish were analyzed (57 species and 7 different diets). And we distinguished 4 different sites: the upstream part of the river defined as reference and the upstream part under the influence of the goldming, the reservoir and the downstream part of the Sinnamary river.

This high level of MeHg newly produced after dams construction impacted fish mercury concentrations. Monitoring of MeHg concentrations in muscle of Hoplias aimara, a piscivorous fish used as mercury sentinel, shows a progressive increase between 1994 and 2007 in the reservoir and downstream river. MeHg concentrations were multiplied by a factor 2 in ten years in the two sites. Levels of mercury contamination analyzed in other fish species characterized by other diets (omnivorous, herbivorous ...) confirmed this trend with contamination 2 to 10 times higher in fish collected in Sinnamary river, according to the diet. In other compartments of the ecosystem the same thing is noticed.

Comparatively to MeHg concentrations measured in H. aimara muscle collected in the main rivers of French Guiana between 2003 and 2006, were significantly lowest than Sinnamary ones.

After 20 years of increase, MeHg in H. aimara muscle seems to point out a decrease in the reservoir and in the downstream river. This decrease is to be compared with the improvement of the physicochemical characteristics of the environment. Indeed decrease of the organic matter concentrations issued from flooded rain forest degradation, lead to an increase of oxygenated water layer in the reservoir. This newly conditions are less propitious to mercury methylation. This tends to show that the influence of the dam on the levels of mercury contamination in organisms might decrease with time and consequently that water quality improves.

MP-103

BASELINE MERCURY CONCENTRATIONS IN SEABIRD EGGS IN LAKE MELVILLE, LABRADOR, CANADA BEFORE FLOODING OF THE MUSKRAT FALLS HYDROELECTRIC DAM

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Nalcor Energy is currently constructing the Muskrat Falls hydroelectric dam on the Churchill River in Labrador, Canada. Flooding of the reservoir began in late 2016. At the environmental assessment hearings which preceded the project, concerns were raised by the Nunatsiavut Government and the Government of Canada about downstream increases in aquatic methylmercury in Lake Melville, as a result of dam construction. This project began in 2013, to determine the baseline mercury concentrations in the eggs of marine birds breeding in Lake Melville, prior to flooding of the Muskrat Falls reservoir. We collected eggs of ring-billed gulls (Larus delawarensis) and common terns (Sterna hirundo) on islands in western Lake Melville in 2013-15. These eggs were analysed individually for total mercury, and in 2015 for stable carbon and nitrogen isotopes (δ13C and δ15N, respectively). We found no differences in mean egg mercury concentrations among islands or among years for either ring-billed gulls or common terns. The geometric mean of egg mercury concentrations in common tern eggs (0.92 μg/g, dry wt.) was significantly greater than in ring-billed gull eggs (0.77 μg/g), while the variance in mercury concentrations was greater in the gull eggs. In eggs collected in 2015, δ15N was analysed to investigate the trophic patterns of the gulls and terns. Comparing δ15N data (mean ± SD) between ring-billed gull eggs (10.5 ± 1.3‰) and common tern eggs (12.5 ± 0.5‰) indicated that the gulls foraged over a wider trophic range, and on average at a lower trophic level than the terns. Mercury concentrations in the gull eggs were unrelated to either δ13C or δ15N. However, in the common tern eggs, both δ13C and δ15N were negatively associated with mercury concentrations. Current mercury levels in the Lake Melville gull and tern eggs pose little risk to seabird populations. However, the two highest mercury concentrations observed in ring-billed gull eggs were probably associated with adverse effects on reproductive success. This study provides baseline data prior to the flooding of the Muskrat Falls reservoir, which we will use to assess the amount and duration of subsequent mercury increases after flooding.

MP-104

DIETARY METHYLMERCURY AFFECTS COGNITION AND BEHAVIOR IN A MODEL SONGBIRD

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Environmental stressors can negatively affect avian cognitive abilities, potentially reducing fitness, for example by altering response to predators, display to mates, or memory of locations of food. We expand on current knowledge by investigating the effects of dietary methylmercury on avian cognition. Captive zebra finches (Taeniopygia guttata) were dosed for their entire lives with sub-lethal levels of mercury, at the environmentally-relevant dose of 1.2 parts per million. In our first study we compared the dosed birds to controls of the same age using tests of three cognitive abilities: spatial memory, inhibitory control, and color association. In the spatial memory assay, birds were tested on their ability to learn and remember the location of hidden food in their cage. The inhibitory control assay measured their ability to ignore visible but inaccessible food in favor of a learned behavior that provided the same reward. Lastly, the color association task tested each birds ability to associate a specific color with the presence of hidden food. Dietary methylmercury negatively affected spatial memory ability but not inhibitory control or color association. Our second study focused on three behavioral assays not tied to a specific skill or problem-solving: activity level, neophobia and social dominance. Zebra finches exposed to dietary methylmercury throughout their lives were subordinate to, and more active than, control birds. We found no evidence that mercury exposure influenced our metric of neophobia. Together, these results suggest that mercury selectively harms neurological pathways that control different cognitive abilities in birds, with complex effects on behavior and fitness. Monitoring schemes can use behavioral endpoints for detecting effects of toxicants, and risk assessment should consider the potentially grave impact of cognitive problems caused by contaminant exposure. For example, many birds store their food for later retrieval, live in complex social hierarchies, and migrate using memory of spatial landmarks. Mercury exposure would severely compromise these ecological functions, even if it had no effect on commonly measured endpoints such as nesting success or body condition.

MP-105

MERCURY CONDITION ASSESSMENTS FOR U.S. NATIONAL PARKS AND APPLICATIONS FOR RESOURCE MANAGEMENT

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The U.S. National Park Service (NPS) safeguards over 400 special places for the protection of unique natural resources and scenic beauty. As a nation, we have promised to leave national parks in an unimpaired condition so that they will continue to provide services such as decomposition, climate regulation, and biodiversity maintenance, as well as serving the educational, recreational, and spiritual needs of society. Yet in many parks, stresses including those from mercury (Hg) have degraded resources. Research and monitoring efforts across the 84 million acres represented by NPS units include assessments of Hg in insects, fish, birds, snow, and air. Although celebrated as some of the most pristine ecosystems in the U.S., this research provides persuasive evidence that Hg may currently be impacting national park resources, and that Hg reductions are likely needed in order to meet the NPS mission to protect these resources for future generations. Even protected areas such as national parks are subjected to Hg contamination because it is delivered through atmospheric deposition, often after long-range transport. Understanding the risk of Hg contamination in NPS units is a challenge because deposition loads and accumulation in the food web are decoupled; elemental or inorganic Hg must first be converted to methylmercury (MeHg) in order to equate to ecosystem harm. Since 2015, NPS has been operating under an interim guidance for Hg condition that incorporates interpolated concentrations of Hg deposition, based on the Mercury Deposition Network, and predicted concentrations of MeHg in NPS surface waters, based on the U.S. Geological Survey (USGS) Methylmercury Model. While this spatial analysis can be used to determine Hg status in parks, it is a rough estimate of condition. Resource condition assessments are supposed to provide direction to park management for each NPS unit. So, to more accurately calculate Hg condition or status in parks, the NPS worked with USGS to: (1) complete a research synthesis identifying Hg toxicological benchmarks on wildlife, and (2) compile a dataset on Hg levels in biota from NPS units. These data are being used to compare measured Hg concentrations in park wildlife with established thresholds, generating park-specific condition assessments. Where park-specific biological exposure data do not exist, the condition defers to the interim guidance. This novel approach provides better understanding of the Hg issue across our national parks, supports park planning processes, prioritizes research needs, drives policy, and fosters more informed management decisions across our protected landscapes.

MP-106

CAROLINA WREN REVISITED: THE CHALLENGES OF FIELD STUDY

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We analyzed the study design and data used to model a predictive relationship between blood mercury (Hg) concentrations and reduction in nest success of Carolina wren (Thryothorus ludovicianus) (Jackson et al. 2011), which has been considered for use in assessments of ecological risk and natural resource damages. Our analysis indicated that the study design and data interpretation were insufficient for predicting reduction in nest success at specific blood Hg concentrations. The reference site selection process was not documented, the number of samples was small (i.e., only two and four abandoned nests at reference and contaminated sites, respectively, in the 2010 dataset of 40 nests used in the predictive model), and the mixed use of artificial (box and tube) and natural nests (with natural nests disproportionately used in reference sites in 2010) confounded interpretation. In addition, the 2010 dose-response relationship between blood Hg and reduction in nest success was biased by the exclusion of two predated nests upstream (because blood Hg data was lacking) and inclusion of one parasitized and three predated nests downstream. We used the mathematical model MARK, similar to MCestimate used by Jackson et al., to evaluate statistical models explaining observations. Our modeled results based on analysis of abandoned nests indicated that cavity type was an important covariate, along with location.We also calculated 30-day nest success using Mayfield estimation. For the pooled 2007 to 2009 dataset where all but one cavity was artificial (and therefore cavity type was controlled), 30-day nest success based on abandoned nests was the same at reference and contaminated sites. In 2010, 30-day nest success based on abandoned nests was higher in the reference sites than in the contaminated sites and higher than both in 2007-2009, however the reference sites had twice as many natural cavities as the contaminated sites. While nest success data and mathematical models have potential for assessing contaminant impacts, robust studies require extensive data collection and accounting for multiple factors other than contaminants that impact nest success and, perhaps more importantly, fecundity. Variable results among years indicate the need for multi-year studies. Mathematical models are powerful; however, conclusions are ultimately limited by the quality and quantity of observations. The Jackson et al. predictive relationship between blood Hg and reduction in nest success is compromised by its study design and small dataset, and therefore should not be used for quantitative estimation of risk, injury, or service loss to songbirds.

MP-107

Declining Hg concentrations in prey fish in Onondaga Lake following sediment remediation

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Onondaga Lake in Syracuse, NY is a 12 km2 lake that has been impacted by a long history of municipal and industrial activity, including two former mercury cell chlor-alkali plants. Since 2004, the lake has experienced significant improvements in water quality following upgrades to the Metropolitan Sewage Treatment Plant that significantly reduced phosphorus and ammonia concentrations in the lake. In addition, in accordance with the Consent Decree for the Onondaga Lake Superfund Site, nitrate addition to the hypoliminion to limit methylmercury release from profundal sediment has occurred annually since 2011, and dredging and capping of contaminated sediment was completed by Honeywell in 2016. Mercury concentrations in prey fish samples have been monitored since 2008 to provide baseline data and to evaluate the effect of the remediation on lower levels of the food chain. Three composite samples of small prey fish by species were collected annually from each of eight locations in the lake and analyzed for total mercury. The locations were selected to represent various sediment management areas with a range of mercury concentrations in sediment. The predominant species were Banded Killifish with occasional collections of Round Goby, Golden Shiner, and Brook Silverside. Alewife were also collected. Under baseline conditions prior to sediment remediation, mercury concentrations in prey fish were approximately 0.31 mg/kg in areas with elevated mercury concentrations in sediment and 0.14 mg/kg in areas on the opposite side of the lake from former discharge points. Following sediment remediation, mercury concentrations in all areas were similar to those observed on the opposite side of the lake under baseline conditions. Reductions in mercury concentrations in prey fish are expected to result in reduced concentrations in upper trophic level fish, although the timing and magnitude are subject to multiple factors including their relative consumption of planktivorous and benthivorous prey fish.

MP-108

LONG-TERM MONITORING OF MERCURY IN SONGBIRDS IN THE NORTHEAST OF THE UNITED STATES

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Mercury (Hg) contamination in aquatic ecosystems is known to pose reproductive and health risks to biota. In past studies, we found high levels of Hg exposure in salt marsh obligate bird species, suggesting that high degrees of bioaccumulation and biomagnification occur in these ecosystems. What is currently unknown are the annual trends and variance seen in biota Hg levels. Invertivorous songbirds, such as the above species are now recognized as best indicators of mercury in the salt marsh ecosystems, where methylmercury (MeHg) biomagnifies in the food chain to levels that can adversely affect reproductive success. With changes to Hg emissions regulations, understanding how MeHg bioavailability changes over time in biota is important. To assess annual mercury changes in mercury exposure of salt marsh songbirds, we non-lethally sampled blood and feathers from several species: Nelsons Sparrow in Maine, Saltmarsh Sparrow in Maine, Massachusetts and New York and Seaside Sparrow in New York to detect and assess Hg changes over time in the same study areas. We analyzed over 13 years of blood and feather mercury data collected from saltmarsh-breeding birds across the Northeast, as a result of multiple projects from 2001 to 2016, to quantify magnitude and trends of mercury exposure for these three species of conservation concern. We found that Hg concentrations are significantly different by site, species, and individual age and temporal trends vary by location after time of sampling has been accounted. Many locations show decline in Hg exposure over the study time period while fewer are stable or increasing. As a result of these projects; 1) we identified several hot spots of mercury in the northeast: (2) we evaluated temporal trends in songbird mercury exposure in northeastern salt marshes.

MP-110

SPATIAL AND TEMPORAL VARIATION OF MERCURY IN GREENLAND HALIBUT (REINHARDTIUS HIPPOGLOSSOIDES) IN THE NORTHEAST ATLANTIC – A COMPREHENSIVE BASELINE STUDY OF A CIRCUMPOLAR SPECIES

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Greenland halibut (Rheinhardtius hippoglossoides) is a circumpolar, Arctic flatfish distributed in both the Atlantic and Pacific Oceans. This species is a cold and deep-water organism, living at depths between 400 and 2000 m and exhibit bathypelagic behavior. Greenland halibut is also an important fishery resource in the Barents Sea and the Norwegian Sea, although the fisheries have been strictly regulated since 1992. In 2006, it was reported that values of mercury in a consignment of this fish were greater than the EU maximum level of 0.5 mg Hg/kg.

Based on risk factors for bioaccumulation of toxic substances, the Greenland halibut was therefore chosen for a comprehensive baseline study to evaluate the food safety status along with cod, saithe, herring and mackerel. The major substances for concern have been mercury along with dioxins and dioxin-like PCBs, which have scientifically based tolerable weekly intake values (TWIs) and also have maximum levels for trade in Europe.

In the baseline study, 1288 Greenland halibut were collected from 27 different positions in the Barents Sea and the Norwegian Sea between 2006 and 2008. Additionally, follow up studies in the Norwegian Sea have been performed for five more years, most recently in 2015. The overall mean of mercury concentration in the baseline study was 0.22 mg Hg/kg wet weight, which is one of the highest recorded mercury concentrations in the North East Atlantic. Furthermore, 99 out of 1288 halibut (7.7 %) showed values greater than the maximum level of 0.5 mg Hg/kg.

Mercury concentrations in this species were size dependent and 44 % of Greenland halibut over 5 kg had concentrations above 0.5 mg Hg/kg while only 2.9 % of those less than 3 kg had concentrations above the EU maximum level. New data analyses and studies have also evaluated the effects of food web dynamics and energy sources on mercury concentrations and bioavailability in this species.

In conclusion, the Greenland halibut is a fish species with relatively high levels of mercury, although the average is below the EU maximum level of 0.5 mg Hg/kg. The size dependent nature of mercury bioaccumulation and spatial variation and integration over time require that Greenland halibut biomonitoring continues to ensure safe consumption of this species by humans.

MP-111

TOTAL MERCURY CONCENTRATIONS IN MULTIPLE TISSUE TYPES FROM BOTTLENOSE DOLPHINS (TURSIOPS TRUNCATUS) STRANDED ALONG THE ATLANTIC COAST OF VIRGINIA, USA

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Marine mammals, such as dolphins, can be exposed to high concentrations of persistent pollutants, including mercury (Hg), due to biomagnification and bioaccumulation. Previous research on marine mammals and other mammalian species indicates that exposure to Hg can negatively impact neurological, hepatic, renal, and immune functions. In cetaceans, skin has been used as a biomonitor of trace element concentrations in the internal tissues of live animals, while liver is the most commonly analyzed tissue for Hg exposure in dead animals. This study aims to evaluate the Hg levels in stranded dolphins from the estuarine and oceanic waters of Virginia, USA and to evaluate the correlations between tissue types. Available tissues were obtained from 128 dolphins that were recovered and necropsied by the Virginia Aquarium Stranding Response Program from 2009-2015. Samples of liver, kidney, muscle, skin, cerebrum, cerebellum, and pons were analyzed for total Hg concentration. Liver samples were found to contain the highest levels of total Hg, followed by the kidney. Concentrations were lower in muscle, skin and brain. Twenty percent of individuals tested had liver concentrations greater than the observed effect level for liver abnormalities seen by Rawson et al. (1993), which suggests that mercury may have impacted liver function in these animals. There was a positive correlation between length and mercury concentration, likely reflecting the bioaccumulation of mercury in older animals. Regressions between tissue types from this study will be presented in order to evaluate the use of skin or liver for estimating concentrations in the other tissue types (kidney, muscle, cerebrum, cerebellum, and pons). Mercury levels in this population will be compared to published studies from Florida, Israel and France in order to evaluate the relative exposure of the different populations. As this is the only study we know of to measure mercury in multiple brain regions of T. truncatus, a comparison of brain tissues will be made and levels will be compared to toxicity thresholds from the literature.

MP-113

TOTAL MERCURY IN DIFFERENT FISH SPECIES CONSUMED IN ARACAJU, MACEIÓ AND SALVADOR-NORTHEASTERN OF BRAZIL

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The determination of mercury in fish tissues are of great concern for public health authorities because of the high potential toxicity. Fish absorb Hg easily and accumulate it in their tissues, and is the main route for human contamination. Even at low concentrations, mercury poses a significant risk to the environment and human health because of its neurotoxic characteristics and its intensive biomagnification. The objective of this research was to determine the concentration of total mercury (Hg-T) in different species of fish commercialized in the markets of the Aracaju, Salvador e Macei cities, in the northeast region of Brazil. The fish species were selected according to their availability in the region and were purchased in local markets from May 2014 to April 2016. Some of the species analyzed were: Catfish (Bagre spp), dolphinfish (Coryphaena hippurus), Acoupa weakfish (Cynoscion acoupa and Cynoscion spp), snapperfish (Lutjanus spp), mullet (Mugil spp), sardines (Sardinella brasiliensis), amberjacks (Seriola spp), and tuna fish (Thunnus spp). A portions of fish muscle tissue was removed from the dorsal-lateral area and lyophilized for 48 h and ground in a processor to obtain homogeneous samples. For the total extraction 0.5 g of dry weight sample was digested with the solution (1H2SO4 + 1HNO3) in a cold finger capped herlenmeyer. The extracts were analyzed by cold vapor atomic absorption spectrometry (CVAAS) with a Lumex RA915+. The mean concentrations found in the species ranged from 136 to 72,331 ng g-1. The highest concentrations were found in tuna fish. This fact can be attributed to its piscivorous feeding habit, confirming the bioaccumulation between different trophic chains. The planktivorous species (sardines and mullets) have the lowest concentration. The total mercury levels presented in this study are below of the maximum permitted by Brazilian legislation for fishery products. In Brazil, the legal limit for Hg content in fishery products is of 500 ng g1 for non-carnivorous fish species. The concentrations found were considered high, in general, the levels of total mercury in the target species do not present great risks for consumers based on the maximum tolerable limits.

MP-114

WATERSHED LEVEL RELATIVE RISK MODELS (RRMS) IN EVALUATING RISKS DUE TO MULTIPLE STRESSORS FOR THE SOUTH RIVER (VIRGINIA, USA)

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Mercury (Hg) release to the South River (SR), Virginia, occurred from a former DuPont plant between 1929 and 1950. Legacy Hg in the potentially impacted areas has been the subject of numerous studies over the last four decades. The South River Science Team (SRST), a multi-stakeholder collaborative program, was established in 2001 to investigate the potential impacts to the aquatic and riparian terrestrial systems along the South River and a portion of the South Fork Shenandoah River (SFSR).

As a part of the SRST Program, a foundational modelling framework was developed based on Bayesian Network-Relative Risk Models (BN-RRMs) for evaluating overall risks from multiple stressors (including Hg and pesticides used in agriculture) and environmental factors (e.g., water quality and habitat suitability). The BN-RRMs allow an integration of competing remedial priorities among different stakeholders, involving risk and ecological services. In addition, the models can be iterative for learn and adapt opportunities, which is consistent with the proposed adaptive management approach for the corrective actions. To support the remedial/risk decisions, the BN-RRMs must reflect the remedial approaches and be consistent with the remedial goals. Five contiguous risk regions were defined, including an upstream reference region, within the watershed along approximately 40 miles of the SR and a portion of the SFSR (10 miles upstream and 30 miles downstream of the former DuPont plant). The risk regions were configured to be as consistent as possible with natural breaks based on land use and hydrogeology, the upstream-to-downstream remedial approach and existing short- and long-term monitoring stations. Baseline relative risk scores were calculated for biotic and abiotic endpoints of importance to the stakeholders (e.g., risks to smallmouth bass and public river use). A series of what-if scenarios were also evaluated to predict the outcomes of potential remedial alternatives.

The results of the modelling indicate that: 1) environmental conditions (e.g., water quality and habitat suitability) are important in considering the overall risk, although Hg is the primary chemical stressor, 2) relative risks vary among the risk regions owing to their spatial differences, 3) remedial measures to mitigate potential risk from Hg may achieve varying degrees of overall risk mitigation due to multiple stressors and factors. These results demonstrate that BN-RRMs are a useful tool to: 1) communicate a holistic approach to risk evaluations, 2) integrate stakeholder priorities in making remedial/risk decisions, and 3) apply adaptive management approaches at complex contaminated sites.

MP-115

IMPACTS OF METHYLMERCURY ON EARLY LIFE STAGES OF A MARINE FORAGE FISH

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Marine and estuarine fish accumulate methylmercury (MeHg) to elevated concentrations, often higher than in freshwater systems. Because MeHg is a potent neurotoxic agent, it is plausible that high tissue concentrations could affect swimming behavior in marine fish which in turn could affect their populations in contaminated waters. We examined sublethal effects of MeHg to a marine forage fish, Sheepshead minnow (Cyprinodon variegatus). Fish were fed a diets comprised of artificial and natural foods (brine shrimp) with varying MeHg concentrations, as high as 4 ppm. The fish were reared on Hg-free and contaminated diets from an age of 5 days until 4 weeks when they reached juvenile stage. Growth rates, swimming activity, response to olfactory cues, and prey-capture ability were tested. Results to date indicate that a MeHg-rich diet has no significant impact on fish swimming activity (swimming speed, acceleration, active time and swimming distance), response to olfactory signals, or prey-capture ability. However, MeHg had a slight impact on the growth rates of these fish.

MP-116

MERCURY ACCUMULATION AND THE MERCURY-PCB-SEX INTERACTION IN SUMMER FLOUNDER

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Patterns in the relative differences in contaminant concentrations between the sexes of mature fish may reveal important behavioral and physiological differences between the sexes. We determined whole-fish total mercury (Hg) concentrations in 23 female summer flounder (Paralichthys dentatus) and 27 male summer flounder from New Jersey coastal waters. To estimate the change in Hg concentration due to release of eggs at spawning, Hg concentration in the somatic tissue and ovaries of 5 of the 23 female summer flounder were also determined. To ascertain whether most of the Hg in the summer flounder was methylmercury (MeHg), whole-fish MeHg concentrations were determined in all 50 summer flounder. Whole-fish Hg concentrations averaged 113 ng/g for females and 111 ng/g for males. Thus, females were 2% higher in Hg concentration than males, on average, but the difference was not statistically significant. Based on Hg determinations in the somatic tissue and ovaries, we predicted that Hg concentration of females would increase by 3.6%, on average, immediately after spawning due to release of eggs. On average, 92% of the Hg in the summer flounder was MeHg. To determine whether the effect of sex on Hg concentration was significantly different from the effect of sex on polychlorinated biphenyl (PCB) concentration, we paired our Hg determinations with PCB determinations from a previous study, and applied regression analysis. Sex significantly interacted with contaminant type (Hg or PCBs), as males were 43% higher in PCB concentration than females, whereas females were 2% higher in Hg concentration than males. Males eliminating Hg from their bodies at a faster rate than females was a likely explanation for this discrepancy between the two contaminant types. Overall, the Hg and PCB concentrations in the summer flounder were relatively low, and therefore our findings also had implications for continued operation of the summer flounder fishery.

MP-117

MERCURY EXPOSURE DECREASES APPARENT SURVIVORSHIP FOR LONG-DISTANCE MIGRANT AVIAN INSECTIVORES

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Elevated blood and tissue Mercury (Hg) is known to cause adverse effects on songbirds. Recent laboratory studies indicate that Hg impairs foraging behavior, immune system function and flight ability. All of these factors can individually or together affect songbird migration success and survivorship in the field. Here we compared Hg level in tail feathers collecting from five migratory songbird species in two age classes (adult or juvenile), migratory distances (long/short migrating distance or resident) and forage guilds (insectivore, omnivore or granivore) in the fall and spring migration season in the same banding location (Long Point, Ontario, Canada) to assess whether the annual return rate was predicted by tail-feather Hg concentrations, which are conserved over the winter non-breeding season. It was predicted that tail-feather Hg in fall would be higher than in the spring, indicating that the individuals with high Hg burden in the fall migration would have lower fitness and thus lower migratory survivorship. Our results suggest that this prediction is borne out for two long-distance migratory neotropical insectivores. Notably, the spring returning cohort of black- poll warbler had almost half of the Hg concentration of those that departed in the fall. We conclude that higher Hg body burden negatively impacts avian insectivore long-distance migration survivorship.

3e: Human exposure and health effects of mercury: epidemiology and population studies

MP-119

SEVERITY OF CHRONIC METALLIC MERCURY VAPOR INTOXICATION IN COMPARISON TO OTHER HEALTH STATES

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Introduction: In artisanal small-scale gold mining (ASGM), a chronic exposure to metallic mercury vapor results from the use of mercury during gold extraction. Health effects such as tremors, erethisms, sleep disorders and many other may occur. The information on health-related quality of life of people suffering from chronic metallic mercury vapor intoxication (CMMVI) is limited. This project analyzed the severity of CMMVI in comparison to other health states.

Methods: International experts, identified by a PubMed search, were invited to participate in a pretested online survey. The questionnaire contained pairwise comparison questions asking if a person with a defined health state is healthier as another person with another health state. Eighteen health states were examined including moderate and severe CMMVI. Data was analyzed with probit regression. Based on the regression coefficients, it was possible to classify the health states according to their severity.

Results: The questionnaire was completed by 105 individuals with expertise in public health, epidemiology and burden of disease among others. Respondents from all continents were reached; however, three-quarters of participants came from Europe. The order of the health states from the lowest (1) to the highest severity (18) was: (1) mild vision disorder, (2) deafness, (3) breast cancer (clinically disease-free stage without permanent sequelae), (4) problems of alcohol drinking, (5) severe asthma, (6) chronic low back pain, (7) HIV/AIDS (seropositive, asymptomatic), (8) mild dementia, (9) diabetes mellitus (uncomplicated/ poorly controlled), (10) manifest alcoholism, (11) coronary heart disease/ severe stable angina, (12) moderate CMMVI, (13) colorectal cancer (stage of diagnosis/primary therapy), (14) stroke (moderate impairments), (15) severe depression, (16) delirium caused by excessive alcohol intake, (17) quadriplegia, (18) severe CMMVI.

Conclusions: The survey results confirm the appraisal of a high severity for both, moderate (rank 12) and severe CMMVI (rank 18) in comparison to other health states. The severe CMMVI, which description contained a worst case scenario of CMMVI, was evaluated as the most severe condition in comparison to the other 17 health states; ranking even higher than severe depression and quadriplegia. The results confirm the necessity to avoid the health impairing exposure to mercury in ASGM. The results can directly be transformed into disability weights to quantify the burden of disease, which will be useful for policy decision making.

This work has received funding from Pure Earth, Bielefeld University, and the European Unions Seventh Programme for research, technological development and demonstration under grant agreement No 603946 (HEALS).

MP-120

IS PHARMACEUTICAL USE ASSOCIATED WITH MERCURY EXPOSURE? AN EPIDEMIOLOGICAL INVESTIGATION USING U.S. NHANES

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Pharmaceuticals & personal care products (PPCPs), while intended to improve health, may have unintended health effects and are emerging contaminants of concern. One potential example which has received limited attention is the effect of PPCPs on the risks associated with exposure to common environmental contaminants such as mercury (Hg). Here, the objective was to understand if pharmaceutical use can be associated with biomarkers of Hg exposure (total blood Hg). We analyzed prescription drug use and Hg biomarker data from the U.S. National Health and Nutrition Examination Survey (NHANES) 2009-2010 (n=7990), accounting for age, sex, income, race/ethnicity, red blood cell count, hemoglobin, and fish consumption. Preliminary two-sample t-tests suggested that subjects taking any prescription drug had significantly higher blood Hg concentrations (~1.5 µg/l) than those not taking any prescription drugs (~1.1 µg/l). Preliminary t-tests on broad categories of drugs indicated that subjects taking cardiovascular agents had higher blood Hg concentrations (~1.7 µg/l) compared to those not taking cardiovascular agents (~1.2 µg/l), while no difference was found between those taking vs. not taking central nervous system agents or psychotherapeutic agents. In multiple regression analyses, overall prescription drug use was not a significant predictor of blood Hg. More multiple regression analyses revealed that cardiovascular agents ($\beta = -0.166$), central nervous system agents ($\beta = -0.186$), and psychotherapeutic agents ($\beta = -0.151$) were significant predictors of lower blood Hg, after accounting for fish consumption. These results suggest that exposure to certain PPCPs commonly utilized by society may mediate exposures to contaminants such as Hg, though future work is needed to determine the hazards associated with such real-world exposures to chemical mixtures.

MP-122

CORRELATIONS AMONG MERCURY CONCENTRATION, STABLE ISOTOPE RATIOS OF CARBON AND NITROGEN OF AMINO ACIDS IN SCALP HAIR FROM WHALE MEAT-EATERS AND HEAVY FISH-EATERS

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We examined correlations among Hg concentration in scalp hair and stable isotope ratios of carbon (d13C) and nitrogen (d15N) of the constituent amino acids in the scalp hair from heavy fish-eaters. Positive correlations were found between the bulk d13C and bulk d15N values (p<0.01) and between the bulk d15N value and Hg concentration (p<0.01) in the hair samples, while no correlation was found between bulk d13C value and Hg concentration. The d15N values for all trophic amino acids (Ala, Val, Leu, Ile, Pro, Asx and Glx) increased with increases in Hg concentration (p<0.01), while the d15N value for Thr decreased (p<0.01). The difference in d15N values between Glx and Thr was positively correlated with Hg concentration, showing the highest correlation coefficient (R2=0.773, p<0.01) among the various combinations for amino acids. Thus, the difference in d15N values between Glx and Thr appear to be the best proxies for the estimation of Hg concentration in scalp hair. In contrast, the d13C values for Val and Glx increased with increases in Hg concentraion (p<0.01), while those for Met and Ile decreased (p<0.01). No correlation between bulk d13C and Hg concentraion could reflect inverse changes of d13C in amino acids constituting the scalp hair.

MP-123

MEASURING METHYLMERCURY IN NEWBORN DRIED BLOOD SPOTS

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Dried blood spots (DBS) are collected and archived from newborns shortly after birth in many jurisdictions worldwide and thus potentially represent a cost-effective biomarker to gauge developmental exposures to methylmercury (MeHg). The objective of this study was to: 1) develop a method to accurately and precisely measure MeHg in DBS; and 2) apply the method to characterize MeHg exposures in newborns by analyzing DBS archived in the Michigan Biotrust. Using DBS created in-house with human blood MeHg standard reference material (SRM) from the Institut National de Sant Publique du Qubec (INSPQ), a method was developed to quantify MeHg in as few as two 1/8 DBS punches. The analytical precision of the method, in terms of assaying the SRMs, was generally less than 10% and accuracy was similarly strong when using SRM-based standard curves. Next, we quantified MeHg in 675 DBS samples obtained from the Michigan Biotrust for Health, which is the States newborn screening biobank initiative. In doing so we calculate a median MeHg concentration of 3.7 ug/L with an inter-quartile range (25th-75th) that spans 2.7 to 4.9 ug/L. To our knowledge there is no robust dataset on newborn blood MeHg values to make comparisons with, and as such the results are compared to MeHg measurements taken on cord blood and show some similarities. This study shows that MeHg can be measured in DBS samples, and that the method can be scaled-up to analyze DBS archived from newborn screening programs thus representing a potentially cost-effective means to biomonitoring MeHg.

MP-124

CHARACTERIZATION OF SEAFOOD CONSUMPTION AND MERCURY EXPOSURE IN CHICAGO ASIAN COMMUNITIES

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Background: The Asian population in the U.S. has elevated blood mercury compared with the non-Asian population due to higher frequency of fish consumption. Methyl mercury (MeHg) crosses the placenta and has been shown to affect neurodevelopment as well as cardiovascular risk in adults. East and Southeast Asians in Chicago, Illinois are a growing population that may have elevated health risks from fish consumption

Methods: We conducted a community assessment of Chinese, Koreans and Vietnamese in Chicago consisting of an in person survey of fish consumption and other cultural dietary practices, hair sampling for total mercury, and analysis of fish purchased in Chicago markets for mercury and PCBs.

Results: To date, 282 of 375 planned participants have been enrolled. On average, participants lived in the US for 12.3 years; 96% of the participants were born outside of the US, and 49% spoke only non-English at home. Mean age was 45 years (range 19, 80), 83% were female, 64% were married, and 49% had an annual income of <$20,000. Fish consumption rates differed significantly by ethnic group, with 61% of Koreans consuming fish 3 or more days/week compared to 38% of Vietnamese and Chinese participants. Most of the fish consumed was purchased, but 30% ate locally caught fish at least annually, although less than 50% of those were able to identify the body of water from which the fish was caught. Seafood consumption preferences varied among the ethnic groups and included species with a range of contaminant levels. Tilapia, salmon, bass, pompano, croaker and sole were the most popular among Chinese; while salmon, pompano, catfish, mackerel, and blue fish, and anchovies, mackerel, salmon, tuna and croaker were top choices among the Vietnamese and Korean, respectively. In our previous work we found that 28% of Chicago Asians tested had hair Hg mercury > 1ppm. Hair sample analysis for the current study is on-going and will be presented. Risk factors for elevated hair mercury that will be analyzed include age, sex, ethnicity, BMI, acculturation metrics and seafood consumption rates. We will also evaluate species of fish and cultural fish consumption practices that affect the risk of elevated hair mercury.

Conclusion: This study characterized risk factors for potential adverse health effects to Chicago Asian communities from fish consumption practices. These findings will be used to develop messages to decrease exposure to contaminants while maintaining consumption of healthy nutrients in fish.

MP-126

ELEVATED MERCURY EXPOSURE IN WOMEN OF CHILDBEARING AGE IN AN ARTISANAL GOLD MINING REGION OF THE PERUVIAN AMAZON: A CROSS-SECTIONAL STUDY

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Artisanal small-scale gold mining (ASGM) is the largest anthropogenic source of mercury contamination globally, presenting a risk to environmental quality and human health. Intensive ASGM activity in the Madre de Dios region of Peru results in the release of an estimated 50 tons Hg/year into the environment. Once in the environment, Hg may be biochemically converted to methylmercury (MeHg), which bioaccumulates in aquatic organisms and biomagnifies in fish commonly consumed by local populations. Previous studies report elevated Hg exposure in the human population of Madre de Dios, includin residents of native communities and mining communities. This is the first study to focus on Hg exposure and risk factors in women of childbearing age, a population of concern, living throughout Madre de Dios. After obtaining informed consent, hair samples, a common MeHg biomarker, were collected from 200 women living in six communities throughout Madre de Dios. All study participants were between 18 and 49 years of age and had not moved in the six months prior to sampling. Each study participant also responded to a survey, which collected information on age, diet (including fish consumption), occupation, level of education, and other risk factors. The survey also included questions regarding knowledge of health risks associated with Hg. Hair samples were analyzed for total Hg (THg) concentration following U.S. EPA Method 7473. The mean hair THg concentration was 2.25 ± 2.54 µg/g (range: 0.01 – 30.12 µg/g) and 67 subjects (33.5%) had levels above the 2.2 µg/g exposure limit established by the World Health Organization (WHO). Mercury exposure was not significantly associated with age, educational attainment, residence time, or frequency of fish consumption. Residents of Pilcopata, located at the headwaters of the Madre de Dios River basin and far upstream from ASGM activity, had significantly lower Hg exposure than residents of other all other communities. This suggests that conditions downstream from Pilcopata, such as intensive ASGM activity or eroded soils from disturbed sites, may account for human Hg exposure. Further research is needed to determine the sources of mercury contamination in the Madre de Dios River watershed. Furthermore, the elevated levels of Hg exposure among women of childbearing age indicate that a public health response is urgently needed. Most study participants expressed concern about Hg contamination, but the majority had limited understanding of the health risks associated with Hg exposure.

MP-127

THE ADMINISTRATIVE COVER-UP OF MINAMATA DISEASE PATIENTS; THE DENIAL OF METHYLMERCURY POISONING CASES BY THE JAPANESE GOVERNMENT IN COURT

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The lawsuit of Niigata Minamata Disease filed by victims in 2007 is currently underway in the Tokyo High Court. The Niigata District Court ruling was that only the plaintiffs who have a officially certified patient in their families should be officially recognized as victims and compensated. However, the diagnosis criteria of Minamata Disease established by the government are too strict for many individuals with symptoms of methylmercury poisoning to be recognized. Uncertified patients are not eligible to receive proper compensation. Although the Supreme Court ruled that the criteria should be relaxed in 2004, the Japanese Government has yet to make a change.

In Niigata, two surveys were conducted regarding inhabitants of the Agano River basin in June of 1965. As a result of this, 26 patients were diagnosed with Minamata Disease. The range of mercury levels in their hair was between 52 ppm and 570 ppm. The current WHO neurological risk standard for adult exposure (hair mercury level: 50 ppm) was based partly on evidence gleaned from these surveys. The Japanese Government also claims that 50 ppm is the threshold level of mercury in hair to cause methylmercury poisoning, and denies patients who have lower levels. However, another study conducted in Niigata showed that patients with less than 50 ppm still exhibit neurological signs related to methylmercury poisoning. Despite the above facts, the Japanese Government has not conducted further investigations, nor compensated patients. Thus, Uncertified patients have no choice but file a lawsuit.

MP-128

DEVELOPMENT OF HUMAN HAIR REFERENCE MATERIAL SUPPORTING BIOMONITORING OF METHYLMERCURY

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The purpose of this study was to develop a new human hair reference material supporting human biomonitoring for mercury speciation. The requirement for certified reference materials for assessing mercury is on high with an increasing number of survey research to evaluate the effectiveness of the Minamata Convention. We collected human scalp hair from Vietnamese males from a barber shop in Hanoi in 2016. Special attention was paid to avoid contamination from grinding vessel during the preparation procedure. We prepared 1000 bottles of hair, each containing 3 g, after sieving and blending of the hair powder. Value for total mercury and methylmercury, as well as other trace elements (Cu, Zn, As, Se) will be presented.

MP-129

A META-EPIDEMIOLOGICAL STUDY TO EXPLORE DOSE-RESPONSE AND THRESHOLD FOR MERCURY AND BLOOD PRESSURE IN HUMANS

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Background: Mercury is a global pollutant with potential for multiple adverse health implications. Studies have reported inconsistent findings for the relation of mercury exposure and blood pressure in human populations.

Objective: To conduct a systematic review and meta-epidemiological analysis to explore: (1) The relation of mercury on blood pressure, and (2) Dose-response relationship and threshold for effect.

Methods: A search with relevant keywords was conducted in Pubmed to identify studies. Abstracts and full texts were screened to identify studies for inclusion. Inclusion criteria were human adult populations, mercury exposure, outcome of systolic or diastolic blood pressure or hypertension, and English language. Data were extracted and assessed for quality by two reviewers. Meta-regression and dose-response meta-analyses were performed to explore the impact of study characteristics, mercury dose, population baseline mercury exposure, matrix of mercury measurement, type of effect estimate (i.e. odds ratio, mean difference, correlation coefficient) and exposure estimate (i.e. log-transformed vs. untransformed).

Results: A total of 34 studies were included. These studies were primarily of cross-sectional design and also included case-control and cohorts. Populations exposed to higher levels of mercury were the Inuit from Canada and Greenland, fishermen in Japan and Indigenous groups of the Amazon in Brazil. Lower exposure to mercury occurred mainly in general populations of the United States, Europe, and South Korea. Mercury was measured in various matrices including blood (N = 15), hair (N = 11), and toenail (N = 4). The outcome was defined as either systolic/diastolic blood pressure as continuous measurements or hypertension defined based on blood pressure threshold. The relation of mercury on blood pressure differed by baseline mercury exposure level. The exploration of dose-response and threshold has several methodological uncertainties and limitations due to inadequate reporting.

Conclusion: Considerable amount of data are available on the relation between mercury and blood pressure in adult populations around the world. The association between mercury and blood pressure varies by study characteristics and levels of exposure. Improvement in reporting and advances in methodology will improve the accuracy of dose-response and threshold estimates. These considerations are applicable to many other environmental contaminants and health outcomes.

MP-131

WHAT IS THE RISK? DENTAL AMALGAM, MERCURY EXPOSURE, AND HUMAN HEALTH RISKS THROUGHOUT THE LIFE SPAN

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All dental amalgam fillings contain approximately 50 % elemental mercury by weight. Concerns about health risks due to continual emissions of mercury vapor from this tooth restorative material have been addressed by dentists, scientists, and government authorities worldwide and have resulted in a range of recommended practices and regulations. By reviewing articles collected by a literature search of the International Academy of Oral Medicine and Toxicology (IAOMT) database and the PubMed database, we identify health risks associated with dental mercury amalgam. We present the science of potential harm as applicable to the general population, pregnant women, fetuses, children, and dental professionals. We specifically address genetic predispositions, mercury allergies, Alzheimers disease, multiple sclerosis, amyotrophic lateral sclerosis, and other health conditions pertinent to dental mercury exposure and its toxicity. We conclude that reviews and studies of dental amalgam mercury risk should assess biocompatibility with special consideration for all populations and all risk factors.

Millions of dentists around the world continue to routinely use dental amalgam, often referred to as silver fillings, as a filling material in decayed teeth. As a result, 67 million Americans aged two years and older exceed the intake of mercury vapor considered safe by the U.S. EPA or over 122 million Americans exceed the intake of mercury vapor considered safe by the California EPA. Mercury is a known neurotoxin that can cause harm to humans, especially children, pregnant women, and fetuses. Furthermore, the use of dental amalgam results in substantial quantities of toxic mercury released annually into the environment. Once in the environment, mercury pollution damages animals, plants, and the entire ecosystem, while creating hotspots that last for centuries.

Except for the USA, numerous countries have taken protective actions against this dental material ranging from a general ban in Norway and

Sweden to restrictions on its use in selected populations in Denmark, Estonia, Finland, Italy, Japan, Switzerland, France, Austria, Canada, Finland, and Germany. In December 2016, three EU institutions (the European Parliament, the European Commission and the Council of the European Union) reached a provisional agreement to ban dental amalgam fillings for children under 15 and pregnant and breastfeeding women as of July 1, 2018.

MP-133

MERCURY EXPOSURE AMONG PREGNANT WOMEN IN REGION OF RUSSIA

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The high levels of methylmercury into the human body there is most often due to eating fish and seafood. The local population of the Vologda region traditionally eat a lot of fish from local lakes and rivers. Fish methylmercury levels were high in the last decade in the North-West of the European Russia including the Vologda region. Therefore the local people are at the highest risk of mercury exposure.

Women living in a large industrial city – Cherepovets (n=53) and workers settlement Vokhtoga (n=45) have been screened (the Vologda region) to assess the content of methyl mercury in human hair. The level of mercury in the hair of pregnant women (geometric mean of 0.296 µg/g, the 95th percentile of 1.078 µg/g) in this population is above the average value obtained in the Moscow region (n=120) geometric mean 1.4 exceeds and twice exceeds that on 95th percentile. In this sample, the threshold value recommended by the WHO and the US exceeded with 2.2% and 5.8% of the participants.

MP-135

MULTISCALE EXPOSURE TO MERCURY EMITTED FROM VEGETATION DURING AUSTRALIAN FIRES

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The occurrence of fires can substantially increase the emissions of mercury (Hg) into the atmosphere. Due to its toxicity Hg Emissions from fires has the potential for increased population exposures, put firefighters at risk, as well as influencing the global Hg budget. Despite the high frequency of fire in Australia little focus has been given to understanding Hg emissions and dispersion from Australian bushfires and the potential health impacts. A recent study carried out in the Commonwealth Science and Industry Research Organization (CSIRO) Pyrotron facility involved measurement of Hg emissions from vegetation concurrent with CO and CO2 in order to quantify Hg emission factors (EF) and emission ratios (ER) from Australian vegetation. These Hg EFs and ERs were used to determine the exposure of firefighters and local populations to Hg. Firefighter exposure to Hg was determined using a data base of personal CO monitors collected over the past two years from prescribed burns. An average hourly exposure of 8.0 ng m-3 with a max 1 min peak value of 683.4 ng m-3 was calculated. Exposure of populations from prescribed and wild fires was determined using a CSIRO Chemical Transport Model (CMT) modified to incorporate the Hg emission factor calculated from the pyrotron experiments. A number of case studies of different fire intensities were run to determine the transport, amount of Hg emitted and the subsequent exposure limits. Local population exposures in closest proximity to the fire source showed inhalation exposures to be well below WHO standards. Populations are mostly at risk from indirect exposure caused by the redistribution of mobilised Hg and methylation within the environments.

MP-136

FISH CONSUMPTION SCREENING AS A PREDICTOR OF ELEVATED BLOOD MERCURY IN WOMEN OF CHILDBEARING AGE

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Fish consumption is associated with elevated blood levels of methylmercury (meHg). The developing nervous system is especially vulnerable to exposure to meHg. Messages about safe fish consumption are complex because fish are also a source of beneficial nutrients. Health care providers are sources of credible information to their patients. Screening at a health care clinic for high mercury (Hg) exposure through biomonitoring is not currently feasible. Instituting screening in the form of brief intake question(s) is possible and explored in this work.

Four hundred ninety-nine women age 16-50 from an area in Minnesota with a cultural connection to fishing completed a health care clinic visit which included: brief screening questions, a detailed questionnaire of fish consumption, and blood collection for Hg analysis. Sensitivity and specificity in predicting high blood mercury Hg were calculated for screening and detailed fish consumption questions, and accuracy was examined using receiver operating characteristic (ROC) curves.

Screening questions on meals of total fish and local fish with moderate levels of mercury had high sensitivity but lower sensitivity. Combining responses to both questions increased sensitivity, but decreased specificity.

Responses from the detailed questionnaire were more accurate than screening questions in predicting elevated Hg, and accuracy was slightly improved with a question that excluded salmon, fish sticks and tilapia from total fish consumption.

A brief set of questions that assess total and moderate Hg fish meals can be an effective tool in predicting which individuals are likely to be at risk of an elevated blood Hg, and allow for targeted education by health care providers. Biomonitoring is the most accurate test for determining risk among those frequently consuming fish, however, incorporation into clinical practice would require changes in current health care systems.

MP-137

HUMAN EXPOSURE OF MERCURY AND METHYLMERCURY IN CHINA

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Mercury (Hg) and methylmercury (MeHg) in diet pose health risks for populations. Based on abundant measurements from previous studies in recent years and Monte Carlo simulation, we carried out a Hg and MeHg human exposure study in China. Results showed that rice consumption was the primary pathway of total mercury (THg) exposure for most populations in China due to its large consumption, but the critical pathway of MeHg intake was fish consumption (including marine fish and freshwater fish), especially in North (49% of total MeHg intake), Northeast (69%), East (57%) and South China (52%) due to its high MeHg concentration. Rice was the most important pathway of MeHg exposed in Central (54%) and Southwest China (65%). In Northwest China, wheat was the critical pathway of both THg (45%) and MeHg (64%) intake. Totally, 43% and 10% of Chinese population exceeded the MeHg reference dose of U.S. EPA and JACFA, respectively, and fish consumption contributed the most. Physiologically Based Pharmacokinetic Model (PBPK) for THg and MeHg was applied to evaluate the impact of diet to human body. Although the amount of fish consumption is lower than other main food, higher concentration of MeHg in fish, especially in marine fish, can drive not only higher MeHg exposure but also higher MeHg/THg ratio in blood. As a more toxic form of Hg, intake of MeHg from fish consumption should be paid more attention, while the aquatic environment has been threatened by the anthropogenic pollution in China.

MP-141

BALANCE BETWEEN MERCURY RISKS AND NUTRIENT BENEFITS FROM FRESH WATER FISH CONSUMPTION IN THE NORTHWEST TERRITORIES, CANADA: PRELIMINARY RESULTS FROM A FIRST NATIONS BIOMONITORING STUDY

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Mercury poses public health risks to populations worldwide. National surveys in North America, such as the Canadian Health Measures Survey and the National Health and Nutrition Examination Survey monitor population baseline levels over time. However, in many remote communities where fish is frequently consumed, such as in the Northwest Territories, such baseline levels are largely unknown. There have been numerous fish consumption advisories related to mercury issued over the past decade in this region, potential increasing the health risks posed by dietary transition away from traditional foods. This research is providing human baseline levels of several contaminants, including mercury, and is investigating the role of the consumption of locally-harvested fish on mercury exposure and risk. It is part of a four-year community based biomonitoring project with the aim to investigate the role of country foods for contaminant exposure using a risks and benefits approach.

This Northern Contaminant Program funded project will collect samples in up to 13 Indigenous communities in the Northwest Territories, Canada. The project includes: 1) a participatory approach with communities, 2) hair, blood, and urine collection, 3) dietary questionnaires, and 4) the analysis of numerous contaminants (including mercury) and nutrients (including selenium and healthy fatty acids EPA+DHA) in biological samples. The results herein are based on pilot sampling completed in 2016 in a single community in the Mackenzie Valley of the Northwest Territories (n=21). Despite an extended fish consumption among participants, and the presence of several consumption advisories on nearby lakes, whole blood mercury (GM 0.69 g/L) and hair mercury (GM 0.40 g/g) of participants were well below the relevant Health Based Tissue Guidelines. However, the plasma EPA+DHA levels (GM 67 mg/L) were also relatively low among participants. In contrast, selenium levels among participants appeared moderately higher than the Canadian general population, respectively for 15% and 20% of participants in whole blood and urine. Interestingly, a negative trend was observed between urine selenium and blood mercury. Future investigations will characterize the drivers of mercury, selenium, and EPA+DHA levels among participants.

In the next year, the participation of additional communities will augment these results so they can be used in community-led initiatives that promote traditional food consumption in manners that keeps mercury exposures low while improving nutrition. This project will facilitate future analyses of temporal trends and will shed light on the effectiveness of various policies for the protection of public health against the harmful effects of mercury.

MP-142

MERCURY CONCENTRATION IN BIOLOGICAL SAMPLES OF PREGNANT WOMEN AND FISH CONSUMPTION

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Since 2000, mining industry has been developing progressively and environmental degradation, pollution has become problematic issues in Mongolia. It has been drawing our attention to that information about people who living in the near mercury polluted mining area has consumed river fish extensively. We carried out determination of total mercury concentration in the maternal urine, hair and cord blood of 265 women who delivered birth in 2016. They were recruited from the area of substantial fish consumption and mining. The geometric mercury concentration in the cord blood of the mothers (n=210) who never consuming river fish was 0.16 ng/ml, the mothers (n=40) who consuming once per quarter was 0.24 ng/ml, the mothers (n=15) who consuming at least once per month was 0.38 ng/ml. In the cord blood of the mothers (n=160) who never consuming canned fish was 0.15 ng/ml, the mothers (n=54) who consuming once per quarter was 0.20 ng/ml, the mothers (n=51) who consuming at least once per month was 0.25 ng/ml. In the cord blood of the mothers (n=156) who never consuming seaweed was 0.16 ng/ml, the mothers (n=75) who consuming once per month was 0.19 ng/ml, the mothers (n=34) who consuming at least once per week was 0.25 ng/ml. We observed that there were statistically significantly differences between cord blood total mercury concentration and river fish or seaweed consumption ($p<0.01$). The geometric mercury concentration in the cord blood of the mothers (n=227) who never consuming river fish during the last 3 months were 0.16 ng/ml and hair concentration was 19.5 ng/g. The mothers (n=28) who consuming less than once per month during the last 3 months were 0.31 ng/ml, in the hair was 33.9 ng/g. The mothers (n=10) who consuming at least once per month during the last 3 months were 0.49 ng/ml, in the hair was 89.6 ng/g. In the other hand, there were statistically significantly differences between river fish consumption during the last 3 months and total mercury in the cord blood, and hair ($p<0.01$). Therefore, we need to take part further investigation on organic mercury concentration in the biological samples of people who living higher fish consumption area.

MP-143

HUMAN EXPOSURE TO MERCURY IN THE AMAZON: A CASE STUDY OF THE TUCURUÍ DAM

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Apart from traditional gold mining, other factors, such as river damming, may show the potential to facilitate mercury accumulation in the Amazonian environment. An increased number of dams are in different development or operational stages, occupying about 100,000 km2 (or 3% of Brazil's Amazon forest) and both mercury methylation and bioaccumulation may be increased by submerging terrestrial areas (peatlands, upland soils, and vegetation). Yet, studies of human exposure to mercury in dam areas in the Amazon are scarce. One of the largest dams ever built in the Amazon recently attracted our attention: the Tucuruí Dam in Tocantins River basin, East Amazon, because high methylmercury concentrations has been found in Tucunaré fishes (Cichla sp.) by Rodríguez et al. (2014). Leino and Lodenius (1995) revealed 20 years ago that 45 people living at the main reservoir presented median levels of mercury (up to 51 µg/g) in hair, well above the safe limit (10 µg/g) established by the World Health Organization (WHO). However, no other evaluation with human populations has been carried out to date in this area.

Therefore, the aim of this work has been to assess the mercury exposure of this population and its potential harmful effects. For this purpose, hair has been selected as the study sample since it has been described as a good indicator of mercury levels in the body and it can be easily collected, transported and stored. Strict exclusion/inclusion criteria were applied for the selection of participants avoiding those with altered hepatic and/or renal functions. Mercury species and total mercury content were determined. Interestingly, the levels were relatively higher than those currently shown for human populations highly influenced by gold mining areas in the Amazonian region. The median level of mercury in hair was above the WHO safety limit, with values up to 75 µg/g (about 90% as methylmercury). Although additional studies are needed to confirm the possible magnification of mercury by the dams in the Amazon, our data already support the importance of adequate impact studies and continuous monitoring.

MP-144

DEVELOPMENT OF LOCAL PUBLIC POLICIES FOR THE PREVENTION AND MITIGATION OF MERCURY CONTAMINATION OF RESIDENTS OF MADRE DE DIOS, PERU

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In recent decades the rapid growth of illegal artisanal and small scale gold mining (ASGM) in the Peruvian department of Madre de Dios has had serious impacts on its ecosystems and people. Recent studies have linked massive releases of mining related mercury into the regions atmosphere and waterways (~40 tonnes / yr) with elevated hair mercury levels in an estimated 60-75% percent of the population - with native populations showing the highest levels of contamination. In May 2016, this public health crisis was formally recognized by the declaration of a Regional State of Emergency due to this mercury contamination.

However, despite recent increased awareness of these environmental health risks, government response to recognize and mitigate this public health crisis has been has been slow and limited. This paper describes the development of an innovative strategy centered on the establishment of a state-level multi-sectoral technical advisory group to 1) improve the quality of scientific information on mercury to support regional and municipal level decision-making; 2) support public sector technical response to the mercury state of emergency; and 3) the development of effective activities to mitigate the effects of mercury on local populations. A key success stories include active participation of primary and secondary level teachers to incorporate information on mercury related health risks and students into lesson plans throughout the public school system. This strategy has resulted in measurable increases in the number and quality of government actions and policies resulting in greater public health impact in local populations. Given the strong economic power of ASGM in similar rural sectors in Amazonia combined with weak governance, these experiences can serve as a reference for local actors to provoke and improve environmental and public health policies using integrative and multidisciplinary approaches.

MP-145

MINAMATA DISEASE HAS SPREAD ACROSS SHIRAUI SEA FROM MINAMATA

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[Background] Very few epidemiological or clinical studies have been carried out around Minamata since the discovery of the disease in 1956. Due to this lack of precise clinical and epidemiological examinations, it has always been assumed that Minamata disease was restricted to the seacoast area around Minamata. After October 2004, our group of doctors have been examining residents outside the government's designated area and found they, the residents, had the same symptoms as Minamata disease victims in Minamata city. Only now has the true spread of Minamata disease becoming clearer.

[Methods] Since 2004 we were carried out studies in almost all areas of the Yatsushiro seashore. We studied 10196 medical records (M/F=4846/5350, mean age=62.7±12.0) who had already been examined for Minamata disease between November 2004 and March 2016. 214 residents of a non-polluted area were selected as a control group (M/F=91/123, average age=52.7±15.0). We classified the data of the polluted area by difference in residential area, occupation, age, and so on, and analyzed them. We also compared the data before and after July 31, 2012, when the application for relief of Minamata disease was closed.

[Results and Discussion] The symptoms of Minamata disease which were prevalent in records we studied: numbness of the hands (polluted area about 86-93% / control area 3%), unsteady tandem gait (50-65% / 9%), narrowing of the visual field (21-30% / 1%) in all area. Symptoms of subjects who had moved from polluted area to other areas were the same as those who lived in the polluted area. There were little differences of symptoms among different districts along the Yatshshiro seashore. There were also little differences of symptoms between fishermen and non-fishermen. It is because, as for dietary habits in the polluted period from 1950 to 1970, fish food was prevalent everywhere. There were little differences in symptoms between before and after deadline for the relief, which means that there were still a lot of Minamata disease patients, who had not been diagnosed or not been relieved.

[Conclusion] The spread of Minamata disease is greater than has been supposed up until now.

MP-146

MERCURY CONTAMINATION IN HUANCAVELICA, PERU: COMMUNITY ENGAGEMENT TO SUPPORT ASSESSMENT AND REMEDIATION

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Huancavelica, Peru is among the worlds most mercury-contaminated cities due to 400 years of cinnabar mining and refining associated with the nearby Santa Brbara mine. Located southeast of Lima at 12,000 ft. in the Andes, Huancavelica is the capitol of its namesake department, which is the poorest in Peru. Several assessments using community-based participatory research have identified mercury two orders of magnitude above risk-based screening levels in earthen walls and floors in 75% of the homes studied. This extrapolates to about 3,800 homes in Huancavelica that could be contaminated above risk based screening levels. The predominant manner of release is likely due to historic emissions of both vapor and dust from refining cinnabar in the city. Local surface soil is contaminated with mercury and other heavy metals, and such soil has been used as construction material for over half the homes in the city. Mercury concentrations in wall and floor material, as well as indoor vapor, are above USEPA and World Health Organization standards for chronic exposure and in many cases above USEPA interim removal action levels. Since 2009, community members have been engaged in research design and conduct, educational initiatives, and the remedial alternative pilot study of 2015-2016. This pilot study ranked sixty assessed homes on the basis of level of contamination, and covered the walls with stucco and poured concrete floors in 9 of the most contaminated homes. Vapor concentrations in six homes was measured using a Lumex RA-915 mercury vapor monitor before and after encapsulation. Vapor concentrations decreased on average approximately 60% after completing the remedial action. In addition, encapsulation of heavy metal-contaminated earthen materials significantly decreased the risk of exposure through incidental ingestion of contaminated dust, which also contains arsenic and lead above screening levels. Stucco walls and concrete floors are moderately inexpensive and are a culturally relevant remedy.

MP-147

APOLIPOPROTEIN E GENOTYPES IN RELATION WITH HG, MEHG, AS AND SE LEVELS IN MOTHERS AND THEIR NEWBORNS

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INTRODUCTION: Apolipoprotein E (ApoE, gene APOE) is a lipid binding plasma glycoprotein with central roles in lipid metabolism and neurobiology. Some studies point on its antioxidative, metal-binding and immunomodulatory/anti-inflammatory properties. It has three major isoforms (ApoE2, ApoE3 and ApoE4) encoded by alleles ε2, ε3 and ε4. A large number of studies estimated, that isoform ε4 allele can be associated with different age related disadvantages. Individuals with ε4 variant are supposed to be more susceptible to metal toxicity, including MeHg known to be neurotoxic especially early in life. The purpose of present work was to estimate relations between ApoE polymorphisms and concentrations of selected metal(loid)s (Hg, MeHg, As and Se) in mothers and their newborns, chronically exposed to low or moderate amounts of Hg, mostly through fish consumption during pregnancy.

METHODS: We used samples and metal concentration data-set of Croatian mothers (n=209, aged 19-44y, sampling in 3rd trimester) and their newborns (n=176, sampling at delivery) from a wider prospective birth cohort study PHIME ('Public Health Impact of long-term, low-level, mixed element exposure in susceptible population strata'; EU project 2006-2011). Database consisted of total Hg, MeHg, Se, As, Pb, Cd, Cu and Zn levels in maternal urine, breast milk, hair, peripheral and cord blood, and child urine. Archived DNA extracts from maternal leukocytes and cord tissue were used for APOE genotypisation by TaqMan pre-designed SNP assay for rs429358 and rs7412.

RESULTS: Mothers and newborns were divided in Apo ε4 carriers (genotypes ε3/ε4 and ε4/ε4) and ε4 non-carriers (genotypes ε3/ε3, ε3/ε2 and ε2/ε2). We identified 17% and 20% ε4 carriers among mothers and newborns, respectively. Mothers with allele ε4 have significantly higher concentrations of: i) blood Se, total Hg, MeHg and As; ii) plasma Se, iii) hair Hg. For Se only, the observed associations persisted after taking into account the influence of possible cofounders like seafood consumption, parity, age, body mass index, education, alcoholic beverages and presence of other metals. The same associations will be estimated for cord blood as well, with special interest on MeHg, because of its suggested neurodevelopmental effects.

CONCLUSION: Observed superior Se status in healthy pregnant females with genotypes Apo ε3/ε4 and ε4/ε4 in comparison with Apo ε3/ε3, ε3/ε2 and ε2/ε2 group could be linked to Apo ε4 'beneficial effects early in life'. The presence of detrimental metals in maternal blood did not affect plasma Se level in sense of its decrease.

MP-149

MERCURY EXPOSURE, SERUM ANTINUCLEAR ANTIBODIES, AND SERUM CYTOKINE LEVELS IN THE LONG ISLAND STUDY OF SEAFOOD CONSUMPTION: A CROSS-SECTIONAL STUDY IN NY, USA

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Mercury (Hg) is a well-known neurotoxin, and has been more recently studied specifically as an immunotoxin. In experimental and a few epidemiologic studies, Hg has been associated with distinct cytokine profiles and antinuclear antibody (ANA) positivity, though patterns at lower levels of exposure, typical of seafood consumers with a western diet, are not well characterized.

Seafood consumers (n=287) recruited on Long Island, NY completed food frequency and health questionnaires and provided blood for analysis of Hg, poly-unsaturated fatty acids (omega-3 and omega-6 fatty acids), selenium (Se), ANA, and several cytokines (IL-1β, IL-4, IL-10, TNF-α, IL-17, IFN-γ, and IL-1ra). Logistic and linear regression analyses were conducted to evaluate associations between serum Hg and cytokines and ANA. Adjusted models accounted for gender, age, ethnicity, income, education, smoking, BMI, selenium, omega-3 fatty acids, omega-6 fatty acids, omega-3/omega-6 ratio, and fish intake. Sex-stratified models were also generated with the expectation that immune profiles would differ between women and men.

Median blood Hg was 4.58 μg/L with 90th %ile =19.8 μg/L. Nine individuals displayed ANA positivity at serum titers above 1:80; many of the cytokines were below detection limits, and the ability to detect was used in the logistic regression analyses. In linear and logistic regression analyses, Hg was not significantly associated with any of the seven investigated cytokines or with ANA-positivity.

Therefore, Hg was not associated with altered immune profiles in this population of seafood consumers.

MP-152

MOLAR RATIO OF SELENIUM AND MERCURY IN BLOOD OF RIVERINE PEOPLE IN THE AMAZON: A PROTECTIVE DIET?

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The exposure to mercury in the Amazon has always been surrounded by numerous questions that have not yet been clarified. Studies carried out in the region over the last 40 years showed the existence of populations with median levels of total mercury in blood upper to the levels found in other regions of the planet. Between these were also frequently found average levels above the biological tolerance limit recommended by the World Health Organization. However, epidemiological and clinical studies in these individuals did not show signs of mercurialism. On the other hand, other studies indicates that a diet rich in selenium would have a protective effect on mercury, since selenium would have the capacity to reduce the toxicity of mercurial compounds from an equimolar proportion. In this study, the molar ratio of selenium and mercury of individuals from five riverside communities located in the Amazonian estuary (Vila do Beja, Vila do Conde, Vila de Itupanema, Curuperê and Ilha São João) was evaluated. Blood sampling was performed in 2013 and followed all ethical recommendations. The analyzes were performed by Induced Plasma Coupled Mass Spectrometry (ICP-MS). The results showed higher mean levels of total mercury in Ilha São João (6.155 μg.L-1), noting that the highest weekly frequency of fish consumption was also recorded. Total selenium levels ranged from 459.882 to 802.199 μg.L-1. The equimolar ratio showed that the amount of selenium atoms absorbed was 238 to 469 times greater than the amount of mercury. It should be noted that the mean levels of total mercury in the blood of these communities were lower than in other areas of the Amazon, a fact that may be associated with greater proximity to the estuary and greater distance from the gold mining areas in Brazil and in border countries. Considering that blood represents a recent absorption of selenium and mercury associated with dietary habit this equimolar ratio was indicative that the diet of these individuals is as rich in selenium as in mercury. This discussion could be extended to evaluate the equimolar ratio of selenium and mercury in other areas of the Amazon and could contribute to a better understanding of mercury exposure in the region.

MP-153

MERCURY EXPOSURE IN AMAZON INDUSTRIAL AREA

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Mineral exploration in the Amazon is old and was intensified in the 70's and 80's. At that time, artesanal gold mining was initially predominant, and soon afterwards large mineral plants were set up to exploit aluminum, copper, iron and manganese. In parallel, large hydroelectric dams were built and industrial poles created to promote regional development. All of these great ventures were always tied to major conflicts of land use and intense migratory processes. The margins of any planning, these industrial areas have settled alongside communities, some of these traditional ones (riverine, quilombola and indigenous), and others have been created over the years, as it happened in the industrial area of Barcarena, located in Amazonian estuary. Industrial production generates atmospheric pollutants containing metal contaminants such as mercury (Hg), causing the environmental exposure of people living near, depending on factors such as the proximity of the ventures and direction of the winds. This study aims to analyze the concentration of total mercury in human blood close to the industrial area and was carried out in the human population of five communities located in the municipality of Barcarena, Pará State, Brazil, in the year 2013. The study was epidemiological and laboratorial and complied with all ethical principles involving human research. The total mercury (THg) analyzes were performed by mass spectrometry coupled with induced plasma (ICP-MS). The THg median levels in the Bairro Industrial, Dom Manoel, Acuí, Bairro Canaã and Laranjal were, respectively, 8.6 μg.L-1, 6.2 μg.L-1, 3.7 μg.L-1, 2.3 μg.L-1 and 0.8 μg.L-1. The increase in HgT values in the communities was positively related to their proximity to the industrial area of Barcarena. The Bairro Industrial and Dom Manoel are communities close to the kaolin industries and coke production, while other communities are further away from sources of pollution. Highlighting the occurrence of low weekly frequency of fish consumption among all communities (1 or 2 times per week). In the industrial processes of extraction and production are released particles easily carried by the air, and these can reach long distances. As evidenced by the significant Hg levels in the communities Acuí and Bairro do Canaã that are further away from the companies in question. The data showed another form of environmental exposure to mercury in the Amazon associated with the proximity of communities of industrial areas.

MP-154

MERCURY LEVELS IN BLOOD ASSOCIATED WITH WEEKLY FREQUENCY OF FISH CONSUMPTION IN THE AMAZON

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Human exposure to toxic and harmful metals occurs naturally and anthropic for thousands of years. These toxic metals are present in soils and rocks, but also as constituents of industrialized products used in our daily lives. The Amazonian riverside populations present a diet based on fish consumption and through this bioaccumulate mercury. Thus, these individuals are environmentally exposed to mercury. The study area comprised the cities of Abaetetuba and Barcarena, located in the Pará State, Northern Brazil. The method was epidemiological and laboratorial. In the year of 2013, blood samples were collected in six riverside communities. All ethical criteria were met and epidemiological forms were completed. Mercury (Hg) was quantified by cold vapor atomic absorption spectrometry (CV-AAS) and mass spectrometry coupled with induced plasma (ICP-MS). Mean blood Hg levels were highest in the Maranhão (10.350 µg.L-1) and Ilha São João (6.155 µg.L-1) communities. In these communities there is a higher weekly frequency of fish consumption (more than 5 times per week). In other communities, such as Vila do Conde, Itupanema, Curuperê and Vila do Beja, Hg levels were similar. In these, for the majority of the population, the weekly frequency of fish consumption is small (at most 2 times a week). The fish of the Amazon region are known for the high concentration of mercury, especially predators. Therefore, when it is consumed by these populations, the tendency is that the levels of Hg in the blood are higher, according to the observed results. The data showed that there is a greater environmental exposure to mercury associated with higher consumption of fish and there is a need for establishing public policies to guide the populations of the region.

MP-155

EPIDEMIOLOGY OF MERCURY EXPOSURE IN THE BRAZILIAN AMAZONIAN BORDER AREA, ACRE STATE

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Natural and anthropogenic processes represent the sources of mercury that can reach living organisms, including humans, through exposure routes. The mercury levels in individuals from areas affected by anthropogenic sources may exceed reference values for biological tolerance to the toxic agent; however, some areas without anthropogenic sources present mercury levels in populations above the reference limit for non-exposed individuals. This is the case of cities in the Acre State in Brazilian Amazon such as Manoel Urbano, where a preliminary study in the first half of the 2000s indicated the possibility of high exposure to mercury in these individuals. This city is located near the border of countries like Peru and Bolivia. To confirm or not the mercury exposure in this city on the bank of the Purus River, a study approved by the research ethics committee was carried out in 2012, which included an epidemiological survey (n = 276) with sampling of human blood and hair and also fish muscle from the Purus River, for analyzes of total mercury and methylmercury, which were developed by Cold Vapor Atomic Absorption Spectrometry and Gas Chromatography with electron capture detector, respectively. The results confirmed a broad spectrum of mercury exposure in the population, ranging from 0.49 to 138.64 µg.L-1 (median of 9.61 µg.L-1) in blood and 0.10 to 41.82 µg.g-1 (mean 2.90) in Hair, associated with fish consumption, age and length of dwelling. Methylmercury levels ranged from 0.37 to 134.19 µg.L-1 (median of 9.45 µg.L-1) in blood and 0.68 to 36.24 µg.g-1 (median 5.63 µg.g-1) in hair. The total mercury levels in fish varied from 0.034 µg.g-1 in non-carnivorous to 6.371 µg.g-1 in carnivorous species. The results indicate the environmental availability of mercury in fish as a way of exposing the population and highlight the importance of transboundary circulation of mercury through international rivers such as the Purus and the contribution of the diversity of mercury sources in the region. Other studies are under way to assess the dynamics of this exposure and to intensify health surveillance actions.

MP-156

INCREASE OF MERCURY LEVELS IN THE SURFACE WATERS OF THE AURÁ RIVER FROM LEACHATE OF LANDFILL

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In most Brazilian cities the solid urban waste is not segregated and disposed on the ground forming open dumps. On the action of intemperic factors are generated liquid effluents rich in contaminants and pathogens. Between this contaminants are toxic metals such as mercury (Hg). The leachate penetrates the soil, contaminating the underground aquifers or are spill into the rivers. In the Belém Metropolitan Region (BMR) for almost 30 years all garbage produced was deposited in the Aurá dump. Near is located the watershed of the Aurá river where a riverine community resides. The Aurá river basin receives both the slurry load and the sewage from nearby districts. In this study, mercury levels were evaluated in surface waters of 5 points of the river Aurá and its tributaries and for control 2 points in the Uriboquinha river and 3 points in the Uriboca river. The samplings were performed quarterly between the period of October / 2014 to July / 2016. The total mercury (THg) analyzes were performed by mass spectrometry coupled with induced plasma (ICP-MS). The results showed that the THg average levels in the surface waters of the Aurá river were higher when compared to the other rivers evaluated. The highest mean value of HgT was recorded in the Santana do Aurá Igarapé (0.32 µg.l-1), the nearest point and impacted by the leachate from the open dump, the lowest value was recorded on the Uriboca river (0.20 µg. L-1), a point distant about 6 km from the source of anthropic pollution. These results show the susceptibility of riparian communities, even from urban centers, to water pollution due to the lack of planning for the proper disposal of solid urban waste.

3g: Occupational mercury exposure from ASGM and other activities

MP-158

THE GENOME OF A MERCURY RESISTANT PSEUDOMONAS ISOLATE REVEALS THE CUMULATIVE ACQUISITION OF MULTIPLE METAL AND ANTIBIOTIC RESISTANCE GENES

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Mercury resistance in bacteria is strongly correlated with antibiotic resistance. In polluted environments, heavy metal resistance and antibiotic resistance are often spread in bacterial communities by horizontal gene transfer through conjugative plasmids and/or other mobile genetic elements. Therefore, in artisanal and small-scale gold mining (ASGM) where amalgamation continues to play a large role in the gold mining process, mercury pollution may provide an additional driving force for the spread of antibiotic resistance. While this correlation has been widely reported, the specific mechanisms of mutual resistance remain unclear. To better understand this phenomenon, mercury resistant bacteria were isolated from soil samples collected in and around the ASGM community of Tsetsera, Mozambique. Samples were analyzed for total mercury, which ranged from 0.02 to 39.10 ppm. Isolated bacterial colonies were screened for mercury resistance by plating them on agar supplemented to a final concentration of 100 mg/L of $HgCl_2$. Each isolate (regardless or mercury resistance) was also tested for antibiotic resistance to ampicillin (50 µg/ml), kanamycin (10 µg/ml), and chloramphenicol (34 µg/ml). Of the 781 strains analyzed 78% of the 221 mercury resistant colonies showed resistance to at least one antibiotic, while only 51% of the 560 mercury susceptible colonies showed some form of antibiotic resistance. The genome of one of the multi-drug resistant strains, a Pseudomonas species (isolate DRA525) was sequenced and annotated. The 6267580 base pair genome sequence revealed evidence of recent acquisition of several resistance genes suggesting that in areas contaminated with heavy metals, there may be an increased selective pressure resulting in the dissemination of resistance genes to other bacterial species including potential human pathogens. These findings provide a better understanding of how mercury pollution acts as a selective pressure in contaminated environments, which may lead to the spread and maintenance of antibiotic resistance in areas associated with ASGM. Unfortunately, these findings also suggest additional risk factors for the health of communities associated with mercury contamination.

MP-159

TOTAL AND METHYLMERCURY EXPOSURE TO COMMUNITIES WITHIN AND UPSTREAM OF ARTISANAL AND SMALL SCALE GOLD MINING AREAS IN MADRE DE DIOS, PERU

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Artisanal and small-scale gold mining (ASGM) in Perus Madre de Dios (MDD) region has grown rapidly since the early 2000s and is a major driver of mercury (Hg) imports to the region. Hg released during ASGM can be transported to aquatic ecosystems, such the MDD river, where it is transformed to monomethylmercury (MeHg), a bioaccumulative neurotoxin. As a result, fish contamination is an issue of concern for individuals living in riverside communities in the MDD region. Not all communities rely on the MDD river for fish, and therefore Hg exposure likely varies depending on geographical region. In this research, we examined total Hg (THg) and MeHg contents in hair samples collected from residents of the MDD region and performed surveys of dietary consumption. This study was part of a larger cohort study to evaluate the health status of communities in MDD, where ASGM and other factors have prompted rapid population growth in the region and large scale alterations to the tropical landscape. Household dietary surveys and proximal 2-cm segments of hair were collected in 2015-2016 from individuals living in communities that were divided into three distinct geographical regions in MDD: within ASGM activity (n=34), near upriver of ASGM (100-120 km; n=31), and far upriver (220 km; n=24). Hair THg was greatest in near upriver communities (average = 5.75 ug/g ; range = 1.86 ug/g to 10.8 ug/g) relative to communities within ASGM (average = 2.00 ug/g ; range = 0.203 ug/g to 11.9 ug/g) and far upstream of ASGM (average = 3.29 ug/g; range =0.723 ug/g to 6.55 ug/g). In both upriver communities, hair Hg speciation was predominantly MeHg (> 71% in all hair samples), while communities within ASGM had MeHg contents ranging from 8% to 128% of THg. The large variation in the relative MeHg contents for individuals within ASGM likely reflects exposure to multiple Hg sources (i.e. inorganic and organic), whereas the consistently high MeHg percentages in upriver communities suggest that exposure is predominantly through one source, such as fish consumption. These results align with our initial assessment of dietary trends in the region, as individuals within ASGM have been reported to rely on non-fish sources of protein, while those in upstream communities heavily rely on the MDD river for food supply. Ongoing research will examine blood biomarkers for mercury exposure as well as other possible metrics such as polyunsaturated fatty acids for fish consumption.

MP-160

POLYMORPHISMS IN THE GENE ENCODING POTENTIAL MERCURY TRANSPORTER ABCC2 AND NEUROTOXIC SYMPTOMS IN POPULATIONS EXPOSED TO MERCURY VAPOR FROM GOLD MINING

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Mercury is used to extract gold out of the gold-containing crushed ores by forming an amalgam, which is heated, evaporating mercury vapor and leaving a porous sponge gold product. This leads to mercury exposure above the common average of the local population. Uptake, distribution and excretion of mercury in the body are genetically influenced. The differences reported in the manifestation of neurological symptoms of individuals, with a comparable level of exposure to mercury, suggest a genetic component influencing the susceptibility to mercury neurotoxicity.

Genetic variants that have been associated with Hg concentrations in the body have mainly been in glutathione-related genes as glutathione plays a key role in mercury metabolism and elimination, mainly due to formation of a more easily transported glutathione-mercury conjugate. The aim of the present study is to investigate associations between polymorphisms in three SNPs of the potential mercury-transporter ABCC2 gene (rs1885301, rs717620, rs2273697) and severity of mercury-related neurotoxicity.

For the present analysis we included data from former projects addressing exposure and neurotoxicity of inorganic mercury, including 1017 participants from the Philippines, Indonesia, Tanzania and Zimbabwe. To increase the power, we pooled data from Asian and African countries as well as heterozygotes and variant homozygotes of variant genotypes. (GG ref. against GA+AA) The participants were stratified into three exposure subgroups: without mercury exposure from gold mining; living in mercury-contaminated areas; mercury working exposure.

To identify chronic inorganic mercury intoxication we developed a neurological score sum including eight binary coded parameters of the anamnestic, clinical and neurophysiological examination. We used multiple logistic regression models to explore genetic factors influencing theoccurrence of mercury intoxication, and multiple linear regression models to explore genetic factors affecting the grade of intoxication. We adjusted for mercury exposure, age and gender. In both analyses we also examined the effect modification of genetic variants on mercury intoxication by including interaction terms between genotype and exposure to mercury.

We found that ABCC2 genotype variety influenced the neurological performance. For rs1885301, the A-allele carriers in African populations showed significantly worse performance at the pencil tapping test. For rs2273697, A-allele carriers in African and Asian populations showed a significant better performance than G-allele carriers at the pencil tapping test. When including an interaction term between genotype and exposure, for rs2273697 the interaction term in Asia showed, at the pencil tapping test and matchbox test, that GA+AA modifies the effect of mercury exposure and leads to a better outcome.

The outcome should ensure us to investigate the associations between mercury and neurotoxic symptoms depending on the ABCC2 transporter more detailed.

MP-161

GOLD MINING IN ECUADOR: A CROSS-SECTIONAL ASSESSMENT OF MERCURY IN URINE AND MEDICAL SYMPTOMS IN MINERS FROM PORTOVELO/ZARUMA

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Introduction: Mercury is a toxic metal and traditionally used in small scale gold mining. In Portovelo, as the oldest small scale mining area in Ecuador, mercury has been an environmental and health problem for decades and even created an international political conflict. The target of this study was to assess the mercury (Hg) concentration in urine of miners from the Portovelo/Zaruma, Ecuador, to establish a prevalence of high values and to compare it with other ASGM regions.

Methods: Urine samples of 865 gold miners in Ecuador were collected and analyzed for their mercury content, using cold vapor atom absorption spectroscopy. The prevalence of high mercury values (>25µg/ml urine) was estimated.

44 miners with mercury levels >15 µg/l filled in a questionnaire for characteristics and possible confounders and were examined for intoxication symptoms to establish the ten points medical score sum.

Results: The median value was 1.8 µg/l. 78,3% of miners were below the HBM-I threshold (7 µg/l urine) and not at risk of an intoxication. 5,9% of miners exceeded the HBM-II limit (25µg/l urine) and were probable to experience intoxication symptoms. The medical score sum had a range of 2 to 8 points with a median of 6.

Conclusion: The relatively low prevalence of high mercury concentrations shows that the politics and techniques to eliminate the use of mercury are successfully implemented. Further studies are needed to identify factors enabling this process.

MP-162

KNOWLEDGE, ATTITUDE AND PRACTICE OF MERCURY USE IN DEVELOPING COUNTRY

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Introduction: Mercury is a global pollutant and its effective control in the environment will take scientific study, innovative management strategies, and the cooperation among all nations.

Objectives: The objective of the study was to assess the Knowledge, Attitude and Practice (KAP), awareness and performance towards dental waste including mercury management policy and practices among the dental practitioners in Nepal.

Materials and Methods. An epidemiologic survey was conducted among 130 private dental practitioners. The survey form was composed of 32 self-administered Standard questions frame based on knowledge, attitude, and those regarding the practices of dentists in relation to dental health-care waste management. The resulting data were coded and a statistical analysis was done with EpiInfo, SPSS.

Results and Discussion. About 53.2% of the dentists were not aware of the different categories of biomedical waste generated in their clinics and where is the right place to recycle.

Only 24.9% of the dentists correctly said that outdated and contaminated drugs come under cytotoxic waste. 39.6% said they break the needle and dispose of it and only 17.9% use needle burner to destroy it. 39.0% of the dentists dispose of the developer and fixer solutions by letting them into the sewer, 38.4% of them dilute the solutions and let them into sewer and only 4.6% return them to the supplier. About 38.6% of the dentists dispose of excess silver amalgam by throwing it into common bin. 3.0% of their annual patients have complain of urticarial lesions due to filling and it was completely cure after removal of filling.

Conclusion. It was concluded that not all dentists were aware of the risks they were exposed to and only half of them observe infection control practices. Infection prevention and medical waste management procedure is very important to control and make mercury free society in developing country. In this globalization age, medical tourist is booming in developing country as well, so keep in mind with universal laws, our efforts should be awareness and give the guidance to all medical and dental practitioner. This will ultimately makes developing country mercury pollution Free countries.

MP-163

MERCURY HAZARDS AND HOW THE COMMUNITY RESPONSES IN DEVELOPING COUNTRY

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Introduction: Heavy metal like mercury was used directly or indirectly since long ago before it was stopped around the world.Since,the value of the metal and its availability in different use in medical appliances is still one of the burdens in developing country like Nepal.The main uses of mercury are in dental amalgam, sphygmomanometers, and thermometers. The mercury once released into the environment can remain for a longer period. Both acute and chronic poisoning can be caused by it. Half of the mercury found in the atmosphere is human generated and health care contributes the substantial part to it. WHO and UNEPissuednew guideline for health care sector to becomemercury free.

Aim and Methods: To find out the Knowledge,attitudeand practice due to hazards of mercury contact among paramedics and patients.

Results and Conclusion: 938 paramedics and 890 patients were asked in-depthstructured questions about mercury hazards and update knowledge. Overall 18% of the paramedics have no knowledge of mercury-free with respect to 69% of the patients. Around 49% of paramedics have broken mercury thermometer in their career and contact with skin. However, 1.2% patient only have a similar history in theirlife time. 4% of the contamination with mercury having SKIN problems. 32% of the patients still have mercury thermometer and sphygmomanometer in their home with respectof0.6% of paramedics.

The above study showed that Healthcare worker has more knowledge of Mercury hazards than patients groups. However, paramedics have broken the mercury instruments than patients party. Similarly, Paramedics have Mercury free device at home thanpatients groups. It meansawareness, literate people having more knowledge towards its practice making mercury free society in a resource poor country like Nepal.

4f: Science, policy, and regulation: Global to local

MP-164

LABELING MERCURY-ADDED PRODUCTS: HOW TO ENSURE CONSISTENCY IN AN EXPANSIVE MARKET

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Countries around the world have enacted mercury product labeling requirements. The purpose of labeling these products is to: 1) Inform consumers at the point of purchase that they contain mercury and may require special handling at end of life; and 2) Identify them at their end of life so that they can be recycled or safely disposed of.

In the United States there are no national labeling requirements covering all of the mercury products in commerce. Currently, however, the states of Connecticut, Louisiana, Maine, Maryland, Massachusetts, Minnesota, New York, Oregon, Rhode Island, Vermont, and Washington prohibit the sale of certain mercury-added products unless they have a label indicating that the product contains mercury and information concerning proper disposal. These state laws establish standards regarding wording, size, location, visibility, and durability. However, the language in these laws differs slightly. This situation creates challenges for manufacturers who sell their products in multiple jurisdictions, because they must comply with differing (and sometimes conflicting) standards.

The Interstate Mercury Education and Reduction Clearinghouse (IMERC) was created in 2001 to provide ongoing technical and programmatic assistance to states in the United States that have enacted mercury education and reduction legislation, and to act as a single point of contact for industry and the public for information about member states mercury education and reduction programs. Promoting clear and consistent labeling of mercury-added products is a priority of IMERCs.

Recently, IMERC has developed acceptable alternatives that can meet all of the states' specifications for mercury-added lamps. These alternatives are designed to promote consistency. The members of IMERC collaborate on their review and decision making regarding alternative labels for products under the framework of their laws. This poster provides an overview of the purposes for labeling mercury products and IMERCs recent experience with labeling of mercury-added lamps.

MP-165

HOW, FOR THE PAST 40 YEARS, WE HAVE BEEN BREAKING DOWN THE BARRIERS HINDERING MEDICAL RESEARCH INTO MINAMATA DISEASE IN JAPAN

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Over 500,000 people, in the Minamata area, were estimated to have been exposed to methylmercury poisoning caused by the contaminated wastewater released by the Chisso Corporation, between 1932 and 1968. Brought to public notice in 1956, the disease was soon named Minamata disease, and eventually, in 1968, was formally recognised by the Japanese government. Kumamoto University researchers, searching for the cause, studied severely affected inhabitants. The intensity of research gradually diminished but gained momentum again when Kumamoto University performed a large epidemiological study (1971-1972). However, the results were ignored and further research on Minamata disease was reduced. There has been no constructive research into the pollution by the government, at any level.

After 1970, a group of volunteer doctors began going door to door and examining residents in the Minamata area. In 1972, one doctor stayed in a hospital in Minamata to continue research. He and his colleagues discovered that although many inhabitants suffered severely from the effects of the pollution they had not been diagnosed with the disease. In 1974, a clinic, to examine disease victims and to treat infected patients, was established in Minamata. Some research papers, in Japanese, were written.

Fear of being ostracised by the community prevented the majority of residents in the area from being examined for the disease. The symptoms of Minamata disease cover a wide range, from mild to severe and as victims grow older the disease develops slower, and it can be more difficult to detect. We would like to point out three barriers that impeded our research into Minamata disease and how we tried to bypass them: 1. The unwillingness of the government to support research on victims of the disease. 2. A lack of a cooperative environment between researchers. 3. The residents lack of information, fear of ostracisation and the despondency of patients.

From the results of long-term population studies, and more intensive studies that we carried out (1987, 2009, and 2012) we show that health problems have not decreased but continue to appear in a large number of residents. Our research was restricted to subjects who had hoped to apply for relief and because of our findings they were granted compensation. We describe how we unveiled the true situation in Minamata today and explain the problems remaining.

MP-166

RECYCLING AND MERCURY FLOW OF USED FLUORESCENT LAMPS IN KOREA

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It is important to effectively collect and properly manage mercury-containing products such as fluorescent lamps, batteries, dental amalgam, and mercury thermometers and switches after use. In 2015, approximately 120 million units of mercury-containing fluorescent lamps were put on the market in Korea. However, only 41 million units of fluorescent lamps were collected and recycled in the same year. Often times, it is very difficult to quantitatively determine the distribution channels and disposal pathway of fluorescent lamps. In this study, we examined the recycling practice and mercury flow of used fluorescent lamps that are regulated by the extended producer responsibility (EPR) system in Korea. Substance flow of mercury in the lamps was estimated by material flow analysis (MFA). The MFA methodology is an analytical method of quantifying flow and stocks of materials or substance in a well-defined system based on mass balance approach. The data required for this study were collected from literature review, available statistics developed by the Korea Ministry of Environment (Korea MOE), discussion with the experts in lamp recycling industry, survey and field visits to local government and lamp recycling facilities in Korea. Based on the result of this study, it was estimated that in 2015 approximately 1.3 ton of mercury in fluorescent lamps was distributed into household sectors and industrial sectors. In case of household sectors, 2.6 tons of mercury was stocked and 0.53 ton of waste mercury was generated from households. Among the household generation of mercury, 0.45 ton of mercury was collected and recycled, while 0.07 ton was either incinerated or landfilled. In case of industrial sectors, approximately 0.79 ton of mercury in fluorescent lamps was distributed; only 0.06 ton was collected and recycled. More effective collection schemes for used fluorescent lamps should be developed to recover mercury, although in recent years LED lamps are continually replacing fluorescent lamps in households.

4g: Socio-economic challenges of mercury policy implementation

MP-167

MATERIAL FLOW ANALYSIS OF MERCURY-CONTAINING PRODUCTS IN KOREA

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There are a number of mercury-containing fluorescent products (e.g., fluorescent lamps, batteries, switches, thermometers, and dental amalgams) that have been used in Korea. Although the use and amounts of the products are decreasing, large amounts of used or waste mercury-containing products are generated each year. Improper disposal of such products may result in severe human health problems and the environmental impacts. Thus, environmentally sound management of mercury-added products is an issue of concern around the world. In Korea, used fluorescent lamps and batteries were included in the extended producer responsibility (EPR) system in 2003 for recycling and recovery of the waste from consumers and reduction of its impact on the environment. This paper presents material flow analysis (MFA) of mercury-containing products in Korea. Material flow analysis was conducted to examine the flow of mercury in the products. The results were based on field visits to the used fluorescent and HID (High Intensity Discharge) lamps recycling facilities, the review of available literature, and interviews with the manufacturing and recycling facilities, and environmental regulatory authorities. Approximately 3.0 ton of mercury is generated from fluorescent lamps, while 1.8 ton of mercury is originated from mercury thermometer and blood pressure. Based on the results of MFA, a total of 5.3 ton mercury from mercury-containing products should be properly managed and treated in 2015.

MP-168

ASSESSMENT OF SUPPLY AND DEMAND PATTERNS FOR THE CHINA MERCURY EMISSIONS FROM SECTORAL PERSPECTIVES BASED ON INPUT-OUTPUT ANALYSIS

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This paper carried out income-based accounting (IBA) and consumption-based accounting (CBA) combined with emission linkage analysis and structural decomposition analysis (SDA) to calculate embodied and enabled mercury emissions in China, for in-depth understanding of the supply and demand patterns of key emissions sectors and socioeconomic drivers that affected mercury emissions in China. The results show that 7 sectors were identified as key mercury emission sectors in 2012 based on emission linkage analysis. IBA identifies mining and service sectors as major income-based mercury emitters and CBA identifies construction and manufacture sectors as major consumption-based mercury emitters. As for mercury emissions embodied in different final demand categories and enabled by different primary input categories, fixed capital formation contributed 304.1 t of mercury embodied emissions, while employee compensation lead to 182.4 t of enabled mercury emissions in China in 2012. Supply-side SDA indicates that, from 1997 to 2012, primary input structure has large contribution to the mercury emission increase. It brought greater impact on mercury emissions increase than final demand structure based on demand-side SDA. Meanwhile, economic structure change (including primary input structure and final demand structure) reduced the mercury emissions in 2007-2012. The production output structure has different effect compared with the production input structure. Our results indicated that more comprehensive knowledge of supply and demand patterns of sectors could help government formulate better policies to control mercury emissions.

4h: Regional Cooperation to Track Atmospheric Mercury Transport and Deposition: The Asia Pacific Mercury Monitoring Network

MP-170

ATMOSPHERIC DEPOSITION OF MERCURY SPECIES IN GWANGJU, A RURAL AREA IN SOUTH KOREA

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Wet deposition is a significant contributor to the total Hg (THg) and methylmercury (MeHg) in terrestrial and aquatic ecosystems as a process for scavenging atmospheric Hg. While the wet deposition of Hg has been monitored at numerous sites worldwide, only a few studies have been conducted in Asian countriesdespite the fact that Asian countries contribute to ~70% of global anthropogenic Hg emissions with increasing temporal trends. Weekly precipitation samples were collected in a rural area of South Korea, Gwangju, and THg and MeHg concentrations were measured in these samples, from April to present. Ambient concentrations of gaseous oxidized mercury (GOM) and particulate-bound mercury (PBM) were calculated using the statistical model constructed by Chen et al. (2013), based on wet deposition data. The THg in precipitation ranged from 1.7 to 13 ng L-1 (volume weighted mean [VWM] of 4.5 ng L-1), and MeHg ranged from 18 to 98 pg L-1 (VWM of 38 pg L-1). The MeHg fraction in THg (%MeHg) was averaged to 0.85% (0.192.7%). The high degree of precipitation depth in summer contributed to significant wet deposition flux for MeHg (r2 = 0.65, $p < 0.0001$), while the correlation between precipitation depth and THg wet deposition flux was not significant (r2 = 0.23, p = 0.05). Furthermore, modeled GOM + PBM concentrations showed a significant negative correlation (r2 = 0.59, p = 0.0005) with MeHg wet deposition flux whereas no correlation was found between modeled GOM + PBM model and THg wet deposition flux (r2 = 0.04, p = 0.43). These results suggest that the concentration of MeHg in precipitation is relatively constant, and, therefore, its deposition flux is largely dependent on precipitation depth, while THg in precipitation shows a typical washout trend. Stable MeHg concentrations in rainwater could be maintained by rapid methylation and demethylation processes in the atmosphere.

MP-171

WET DEPOSITION AND AIR CONCENTRATIONS OF MERCURY AT A RURAL SITE IN THAILAND

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Mercury has been regarded to be one of the extremely hazardous metals due to its toxicity, volatility and low vapor pressure even at ambient temperature. As such, Mercurys existence is actually everywhere. It is noted that atmosphere is the foremost transport pathway of mercury emission and wet deposition is the most efficient at removing divalent mercury (a soluble form) from the air to the environment. However, there are still limited accessible data of air concentration and wet deposition of mercury in Thailand due to lack of measurements. Therefore, it is important to develop appropriate methods suitable for atmospheric and wet deposition mercury measurements in Thailand.

The poster presents the implementation of atmospheric and wet deposition of mercury measurements laboratory and the initial mercury results at a rural area in Thailand. With guidance and technical supports of Asia-Pacific Mercury Monitoring Network (APMMN), we conduct research and development on methodologies. The sampling and analysis of mercury in ambient air was utilizing Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) based on the Compendium Method IO-5. The determination of mercury in precipitation was by Oxidation, Purge and Trap, and CVAFS based on the Method 1631, Revision E. It is well known that preventing samples from becoming contaminated during the sampling, transport and analysis process constitutes one of the greatest difficulties encountered in trace mercury determinations. The collaboration with APMMNs experts enabled us to improve facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable trace mercury determinations. We conducted measurement of mercury in air and precipitation at the Environmental Research and Training Center which is located in a rural area of Pathumthani province, the suburb of Bangkok. The results showed that mercury in ambient air during June 2016 ranged 1.5-1.7 ng/m3. The mercury level in precipitation samples of one year sampling were varied from 1.0 - 24.5 ppt with the field blank below 0.5 ppt. Continuous monitoring program of mercury in air and precipitation in different areas in Thailand is necessary to understand the characteristic of mercury transport and deposition as well as determining source-oriented mercury changes in Thailand.

MP-172

NETWORK MONITORING OF MERCURY WET DEPOSITION ACROSS ASIA

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One of the most critical measurements needed to understand the mercury biogeochemical cycle is the rate of atmospheric mercury deposition. Atmospheric mercury is thought to be the largest input of mercury to most rivers and lakes globally. Consistent monitoring of mercury deposition provides a method to understand an essential component of the mercury problem at many locations. Tracking long-term deposition trends is particularly important as emissions reductions are realized under the Minamata Convention.

Several cooperators (Environmental Protection Administration-Taiwan, National Central University-Taiwan, National Atmospheric Deposition Program of the U.S., U.S. Environmental Protection Agency, and Environment Canada) have launched the Asia-Pacific Mercury Monitoring Network (APMMN) to systematically monitor mercury in wet deposition and in the air to estimate dry deposition. The APMMN seeks to promote sharing of information, data, and technologies to expand coordinated mercury monitoring capacity, cultivate a common understanding of policy-relevant mercury scientific topics, and develop mercury datasets useful for modeling. APMMN will provide technical assistance to Asia-Pacific countries that have mercury environmental concerns, but have limited mercury monitoring capabilities. Current membership includes ministries in Vietnam, Thailand, Indonesia, Sri Lanka, Philippines, Mongolia, Korea, and Japan. Key network design features include: a common, written standard operating procedure, a quality assurance plan and data flagging procedures, one regional laboratory, and regular operations meetings (http://apmmn.org.tw/). Cooperation in monitoring and data sharing among all participating groups would promote a better scientific understanding of the mercury issue, and would benefit all countries.

Basic observations, thus far, for APMMN will be presented, with comparisons to established networks, and future directions for the APMMN.

MP-173

CONTINUOUS MONITORING ON ATMOSPHERIC GEM, GOM AND PBM CONCENTRATIONS AND WET HG DEPOSITION FLUXES AT FUKUOKA IN THE NORTHERN KYUSHU OF JAPAN

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Atmospheric GEM, GOM and PBM2.5 were observed using the Tekran continuous monitor from December 2013 to November 2014 at Fukuoka City, located in the northern Kyushu islands, Japan. Their concentrations were lower than those at the urban cities in the East Asian region. GEM concentrations had no diurnal and seasonal variations. However, some pollution events were observed more frequently in winter and spring. The pollution events were sometimes occurred when the low pressure system or cold front and the travelling anticyclone passed over Fukuoka City. Back trajectory analysis showed that almost of these events were influenced by the substances transported from the Asian Continent. On the other hand, GOM concentrations were higher in the daytime than in nighttime, especially in spring, which has strong UV irradiation. Therefore, GOM might be mainly produced by photochemical reactions between GEM and air pollutants such as OH radical. PBM2.5 concentrations were higher in winter than in other seasons. Long-range transport from the Asian Continent mainly contributes to the pollution events of PBM2.5. In this study, the Hg in coarse particles (more than 2.5 µm) was also monitored by analyzing Hg in the impactor frit put into the air inlet of the Tekran monitor. About 30% of total PBM was in the coarse particles. Using these observation data, the annual dry deposition flux was calculated at around 10 µg/m2/yr. In addition, it is indicated that the dry deposition flux of PBMcoarse could not be negligible. The annual wet Hg deposition flux was 11.3 µg/m2/yr by calculating from the volume weighted mean concentration (7.7 ng/L) and annual precipitation depth. Thus, the total atmospheric deposition flux at Fukuoka was about 20 µg/m2/yr, which was almost equal with those in the other Japanese urban cities and industrial area.

MP-175

GENERAL TRENDS OF TOTAL MERCURY (TM) WET DEPOSITION IN URBAN AND RURAL AREAS IN KOREA: LOCAL URBAN ACTIVITIES AND REGIONAL-SCALE TRANSPORT OF MERCURY

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Total mercury (TM) was determined in weekly precipitation samples collected in Northern (Seoul, urban), Middle (Taean, rural), and Southern (Jeju Island, rural) Korea, from April 2015 to November 2016, to determine the seasonal variations in TM wet deposition and to assign sources and their contribution to mercury wet deposition. The monthly volume weighted mean (VWM) TM concentrations in Seoul, Taean, and Jeju Island were 22 ± 16, 13 ± 8.4, and 5.6 ± 4.7 ng L−1, respectively and the monthly TM wet deposition flux in Seoul, Taean, and Jeju Island were 1.5 ± 2.0, 0.85 ± 0.60, and 0.66 ± 0.47 µg m−2, respectively. The high VWM TM and TM wet deposition flux levels in Seoul were probably a result of local urban activity. Seasonal VWM TM concentrations in Seoul were highest in winter followed by summer, fall, and spring. The high VWM TM concentration in winter probably reflects the higher coal consumption in winter due to high demands for residential heating in China. The TM wet deposition concentrations in Seoul were influenced by both local urban activities and regional-scale transport. The large seasonal wet deposition fluxes observed in the summers were possibly due to intense monsoon rainfalls. The long-term measurement of TM wet deposition in Korea will go far toward achieving the goal of an Asia-Pacific Mercury Monitoring Network – APMMN.

MP-176

CONCENTRATIONS AND POSSIBLE SOURCES OF ATMOSPHERIC SPECIATED MERCURY IN A REMOTE ISLAND OF KOREA

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Atmospheric mercury mainly exists in three operationally defined inorganic forms: gaseous elemental mercury (GEM, Hg0), gaseous oxidized mercury (GOM, Hg2+), and particulate bound mercury (PBM, Hgp). Sum of GEM and GOM is often called as total gaseous mercury (TGM). GEM accounts for approximately 98% of total Hg in ambient air because its wet and dry deposition velocities are much lower than those of GOM and PBM. On the other hand, GOM is readily removed within a short distance from emission sources. PBM is either directly emitted from natural and anthropogenic sources or formed by gas-particle conversion from GOM. In this study, atmospheric speciated Hg concentrations were measured in a remote island of Korea, located between China and Korea peninsula in order to identify the relative importance of Chinese and domestic sources as well as possible secondary formation. Mercury samples were collected during six intensive sampling periods including August 18-21 in 2015, January 7-13, March 22-26, May 11-17, July 25-August 1, and November 1-8 in 2016. TGM, GOM, and PBM concentrations showed different diurnal and seasonal patterns. TGM and PBM concentrations were high in spring and winter while GOM concentration was enhanced in summer. Conditional Probability Function (CPF) analysis was performed to determine the predominant wind direction associated with high Hg concentration. Backward trajectories using HYSPLIT 4 were also calculated to depict a synoptic wind patterns during sampling periods, and potential source contribution function (PSCF) based on back-trajectories were applied to locate possible source areas. TGM and PBM concentrations generally increased with the winds blown from China in spring and winter. Short-term peaks of PBM concentration were also observed when the winds were directly passed through North Korea. However, high GOM concentration was associated with winds originating from ocean in summer, possibly indicating active oxidation reactions in marine boundary layer. More detailed results on major source/pathway identification will be shown at the conference.

MP-177

PARTICIPATION OF TAIWAN TO THE ASIA-PACIFIC MERCURY MONITORING NETWORK (APMMN)

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East, Southeast, and South Asia are the major anthropogenic mercury (Hg) emission source regions globally. While atmospheric and rainwater Hg monitoring activities have been steady in East Asia (China, Korea, Japan and Taiwan), such activities are limited in Southeast and South Asia due to the lack of monitoring capacity. Regional scientists and decision-makers must rely on limited information to understand and quantify the critical linkages between mercury emissions, environmental response, and potential human health concerns. As such, the Environmental Protection Administration Taiwan (EPAT), National Central University (NCU), U.S. Environmental Protection Agency (USEPA) and National Atmospheric Deposition Program (NADP) worked together since 2012 for the establishment of the Asia-Pacific Mercury Monitoring Network (APMMN) to assist regional countries for capacity building and to systematically monitor wet deposition and atmospheric concentrations of Hg in a network of stations throughout the Asia-Pacific region. EPAT and NCU are committed to this effort and network development. EPAT, with the assistance of NCU, has been supporting regional atmospheric Hg workshops and APMMN workshops in Taipei (2012), D.C. (2013), Hanoi (2014), Minamata (2015), and Bangkok (2016). EPAT funded NCU to establish the Center for Environment Monitoring and Technology and to employ a site liaison to support the coordination and operation of APMMN. The site liaison will travel to partner countries to provide assistance and services if necessary. The Atmospheric Trace Element Laboratory (ATEL) of NCU helps the analysis of total Hg in wet deposition samples from partner countries. To accommodate to future demand, EPAT helped ATEL to expand its analytical capacity by expanding the lab area and equipping the lab with 2 new class-1000 cleaning rooms, a new DI system, 2 Tekran 2600 Hg analyzers, and an autosampler in 2016. EPAT will provide wet deposition samplers (MIC-B type) to support rainwater sampling at sites in partner countries. Besides, ATEL will conduct a side-by-side intercomparison between the MIC-B and N-CON samplers on NCU campus in 2017 to assure comparable data quality between APMMN and NADP/MDN. To assist partner countries in developing their mercury monitoring and assessment capacity, training workshop will be arranged and held by NCU in 2017 to provide training on methods of sampling and analysis of mercury in air and rainwater and may expand to include other media (e.g, water, biota).

MP-178

MERCURY MONITORING IN VIETNAM

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Vietnam has signed the Minamata Convention on Mercury. The Vietnam goverment has approved the convention. A number of plans have been issued for the monitoring of Mercury, as well as the reduction of Mercury production. Vietnam Environment Protection Agency is currently a participant of the APMMN. One sampler has been installed in Hanoi for wet deposition and Mercury monitoring in the Atmospheric. Vietnam is going to establish a Mercury mornitoring network in the future.

MP-179

ESTABLISHING STANDARDIZED PROTOCOL FOR ATMOSPHERIC MERCURY NETWORKS WORLDWIDE

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To compare regional and global atmospheric mercury, standardized methodology, operating practices and data quality assurance needs to be established.

In October 2007, an atmospheric mercury best practices and standard operating procedure (SOP) workshop was held in Chicago, Illinois, USA. The workshop produced an atmospheric mercury speciation SOP distributed internationally for comments. All comments were merged into the document. In 2011, the National Atmospheric Deposition Program quality assurance manager and Atmospheric Mercury Network (AMNet) site liaison separated the document into several smaller, user friendly manuals and SOPs. In Brussels, April 2011, the AMNet site liaison presented the documents to the Global Mercury Observation System (GMOS) where the documents were adopted for use within the network. In November 2016, the Asia Pacific Mercury Monitoring Network (APMMN) organized a workshop on continuous atmospheric mercury monitoring. The APMMN workshop compared Asian Pacific SOPs to those used in AMNet/GMOS (See Suzuki APMMN poster). This poster will outline the development of the AMNet SOPs, manuals, and review the quality assurance and control used to evaluate atmospheric mercury data providing an opportunity to discuss the development and criteria with the NADP AMNet site liaison.

MP-181

CANADIAN ATMOSPHERIC MERCURY MONITORING: ACHIEVING HIGH QUALITY DATA AND DATA COMPARABILITY

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Atmospheric mercury has been monitored in Canada since the 1990s through both ongoing networks and independent research programs. Canada has been part of the Asia Pacific Mercury Monitoring Network (APMMN) since 2012. While many sites have come and gone over the years in Canada, Environment and Climate Change Canada currently monitors total gaseous mercury (TGM) at 11 sites and speciated atmospheric mercury at 5 sites. The mercury data is collected using the TekranTM 2537 and TekranTM 2537/1130/1135 system for TGM and gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate mercury (PHg), respectively. The measurements at each site across the country are collected using the standard procedures developed by the Canadian Atmospheric Mercury Measurement Network (CAMNet). Once collected, the mercury dataare processed through a quality control program that was developed at Environment Canada called the Research Data Management Quality system (RDMQ). All sitesapply the same system and procedures to the collected data. This system is designed to standardize QA/QC procedures by applying predetermined criteria to collected data to identify concentration and instrument fluctuations. The criteria were developed by the users of the Tekran instruments over time and include a variety of instrument, site and operator flags. There are 14 possible different flags applied to the TGM/GEM data and an additional 9 flags applied to the GEM/RGM/PHg data. The RDMQ system was compared with NADPs AMNet QC system and little difference was reported in the final data sets and thus it was concluded that either program could be applied to data emerging from the Tekran instruments.

Considerable atmospheric mercury monitoring data has been collected in Canada for over 20 years. The mercury levels at all but one of the current monitoring sites in Canada are decreasing. These decreases have been, for the most part, attributed to declines in emissions of mercury to the atmosphere. The trends reported in Canada are from high quality data as a result of the efforts that Canadian researchers have made to follow the standard protocols and procedures. Temporal and spatial trends of this monitoring data will be presented to provide an overview of the success of the Canadian mercury monitoring program. The treatment of the data collection and analysis will be discussed and recommendations on the application of this methodology to other potential networks, such as the APMMN, will be discussed.

MP-182

EXPLORING POSSIBILITY OF COORDINATED ATMOSPHERIC MERCURY MONITORING IN ASIA-PACIFIC REGION

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The National Atmospheric Deposition Program, the United States Environmental Protection Agency, and National Institute for Environmental Studies of Japan, co-organized the Asia-Pacific Expert Workshop on Continuous Atmospheric Mercury Monitoring at Minamata city, Japan, from November 28 to December 2, 2016. The objective of the workshop was to share monitoring practices and develop a common understanding of the operation and quality assurance procedures of automatic atmospheric mercury monitoring across the Asia-Pacific region. Researchers and environmental regulatory agencies operating Tekran(r) speciated/continuous monitoring system in NADP/AMNet in North America, and in Australia, Japan, Republic of Korea, Philippines, Taiwan, and Thailand discussed in detail the SOPs (Standard Operating Procedures) and QA/QC processes of their individual monitoring programs. As the result of the discussion, we found that SOPs and QA/QC processes are essentially common in at least 5 programs analyzed. We analyzed QA actions on operation practices in terms of procedures, intervals and other necessary standpoint among the 5 programs. We found that QA practices are essentially common and also action intervals are essentially similar for the purpose to achieve comparable monitoring outputs among the programs. This means that the major part of the actions used by all 5 programs/networks is very consistent each other. Although some procedures need to be discussed further to achieve better consistency, we found no substantial discrepancies among programs that may significantly affect data comparability among all the programs represented. This finding would be a starting point to explore possibility of coordinated atmospheric mercury monitoring in Asia-Pacific region.

1b: Biogeochemical cycling of mercury in the ocean

TP-001

A TIME SERIES OF MERCURY SPECIES IN MONTEREY BAY: IMPLICATIONS FOR SOURCES AND ENVIRONMENTAL FORCING FUNCTIONS

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Approximately 130 water samples were collected at the head of the Monterey Bay submarine canyon for the analysis of dimethylmercury (DMHg),monomethylmercury(MMHg), and total mercury (THg) during a one-year study. Through a bottom-moored seawater intake system, (17 meters depth) measurements of sigma-t, temperature, salinity, oxygen, turbidity, fluorescence, and pH were made concurrently with the collection of each sample. An initial, intensive 30-hour study showedthat variations in DMHg were strongly associated with the undulation of internal wavesand their associated water masses as they were sequentially entrained into the seawater intakes. To avoid aliasing of seasonal fluctuations, this finding led to periodic, twice daily sampling to capture water from above and within thethermocline, a region over which strong gradients in DMHg and MMHg are typically found. In the higher sigma-t strata DMHg and MMHg varied from 0 to 140 fM and 11 to 160 fM respectively, whereas the lower sigma-t strata variations in the species ranged from 0 to 100 and 5 to 112 fM, respectively. When fluctuations in internal wave height are filtered out, a strong relationship between methylated species and upwelling season is observed. THg varied from 373 to 4000 fM, however there was no relationship seen with respect to water mass. pH and DMHg exhibited an inverse relationship where higher pH samples had lower DMHg concentrations. In contrast, higher salinity water showed higher concentrations of DMHg. There is also a strong relationship with apparent oxygen utilization (AOU) and DMHg. In this study we will present mercury concentrations with coastal upwelling indices and examine processes responsible for the degradation of organic mater in the upper water column to understand mercury speciation over the study period and discuss these findings in the context of seasonally forced oceanographic conditions present in thenearshorecoastal environment of the California Current and Monterey Bay.

TP-002

METHYLMERCURY ACCUMULATION IN MESO- AND BATHYPELAGIC FISH OF THE NORTHERN GULF OF MEXICO

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Humans are exposed to toxic methylmercury (MeHg) mostly from the consumption of seafood, particularly top-predator fish (e.g., tuna, swordfish, mackerel) that can accumulate high concentrations of MeHg. A recent investigation has shown that MeHg concentrations in predatory fish of the subtropical North Pacific Ocean increased with greater foraging depth. However, little is known about the MeHg content of smaller fish inhabiting meso- and bathypelagic zones of the ocean. We sampled dragonfish, lanternfish, bristlemouths, and hatchetfish with vertical net trawls at multiple locations in the northern Gulf of Mexico as part of the DEEPEND project. Preliminary results suggest that MeHg concentrations vary widely within and among these fish species. The three species of Myctophiformes fishes that migrate to shallower depths to feed at night have lower concentrations of MeHg than four of the five

Stomiiformes species that do not migrate from depth. Moreover, mean MeHg concentration is positively correlated with average foraging depth among fish species. Differences of MeHg concentrations in prey fish as a function of vertical migration and foraging depth in the ocean provide a mechanism to explain how concentrations in predatory fish increase with greater foraging depth.

TP-003

MERCURY DISTRIBUTION IN THE LABRADOR SEA DURING THE 2014 GEOTRACES GEOVIDE CRUISE

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Labrador Sea is one of the main the entrance into the ocean interior, and the mercury (Hg) cycle in the ocean is heavily impacted by human emissions, it is the reasons why we report here the first high resolution Hg distribution pattern along a transect from Greenland to Labrador coasts performed after the 2014-winter convection. Total Hg concentrations in unfiltered samples ranged from 0.25 to 0.66 pM averaging 0.43 ± 0.1 pM (n = 106). Generally, Hg concentrations increased downward from surface to deep waters, and southward from Greenland to Labrador. Concentrations in filtered samples represented from 62 to 92 % of the unfiltered waters and exhibited a similar distribution. Most striking is: (i) the very low Hg concentrations in the Labrador Sea Water formed during the 2014-winter convection, and (ii) the high Hg concentrations in the waters of the Labrador Current, which receive waters from the Canadian Archipelago and the Baffin Bay.

TP-004

SPATIAL AND TEMPORAL TRENDS OF MERCURY SPECIES IN THE MEDITERRANEAN SEA

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In seawater mercury is a very reactive element. Once in the water, it can be present in different forms: elemental mercury Hg(0), Hg(II) complexes and organic Hg forms (mainly methyl mercury (MeHg) and dimethyl mercury (DMeHg)). Mercury speciation and its distribution in surface and deep waters of the Mediterranean Sea were studied during several oceanographic cruises on board the Italian research vessels Urania and Minerva since summer 2000 as part of different European (Mercyms, GMOS) and national research projects, covering regions from Strait of Gibraltar on the west, and Levantine Sea on the east, as well as Adriatic Sea with the Gulf of Trieste as Mediterranean most northern part. The study includes deep water profiles of dissolved gaseous Hg (DGM), reactive Hg (RHg), total (THg), monomethyl Hg (MeHg) and dimethyl Hg (DMeHg), and with some water quality parameters in coastal and open sea deep water profiles. Recent studies in the Mediterranean Sea revealed the presence of enhanced Hg emission rates and/or more active atmospheric transformation processes in this region due to a number of climatological, meteorological, geographical and geological features that characterize the basin.

Concentrations of measured Hg species were characterized by seasonal and spatial variations. Relatively high portions of DGM indicate high reactivity of Hg in open marine waters. DGM was present in surface waters mainly as Hg0 as no DMeHg was detected, while towards the bottom a noticeable, but relatively small portion of DMeHg (<5 %) is present in most of the Mediterranean. In Adriatic DMeHg was present in higher fraction and was detected in surface waters, but in very low concentrations. DGM generally increases with depth, suggesting a source of volatile Hg in deeper waters. Average DGM concentration was the highest in deep water masses (WMDW and EMDW). From certain profiles it is possible to observe that increase of DGM corresponds to a decrease in dissolved oxygen levels, suggesting that DGM is produced by biologically mediated processes in the oxygen minimum zone. The observed decrease towards the surface is a result of the balance between production and loss processes on boundary between water and atmosphere.

TP-006

SEA SURFACE MICROLAYER CONCENTRATES MONOMETHYLMERCURY: IMPLICATIONS FOR MERCURY CYCLING AND TRANSPORT TO LAND

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Monomethylmercury (MMHg) was measured in the sea surface microlayer (SML), an operationally defined 10-100µm thick film typically enriched in organics and normally associated with high concentrations of hydrophobic constituents (hydrocarbons, PCBs, carbohydrates and pesticides). In 2015, two cruises along the California Coast, SML samples were collected from a small workboat, using an acid cleaned glass plate and glass tubes. Samples were analyzed via gas chromatography (GC) coupled with a Tekran© Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) Model 2500 Mercury Detector. SML values for MMHg ranged from 16.02 - 380.39 fM, corresponding to enrichment factors (EF) of 2.5 – 29.6 relative to underlying water from the mixed layer. These represent the higher end of other trace metal enrichments in this microenvironment and are the first such measurements to our knowledge. The lipophilic nature of MMHg likely lends to its partitioning into the hydrophobic organic material of the SML. Adsorbtion of MMHg onto buoyant bodies such as microplastics, fish eggs and larvae, also present in the SML, may serve as entry into the food web through ingestion. MMHg EF of the SML correlated strongly with temperature (n=7 r=0.7229, p = 0.0665). Higher sea surface temperatures can be indicative of stratification in areas of downwelling, which concentrate substances and objects floating at the surface. Based on calculated values, these trace metal sampling techniques likely yield enriched, yet still diluted samples (due to method associated dilution of the method itself). Aerosolization of MMHg laden SML could create more concentrated MMHg marine-derived aerosol particles, and are potentially a more accurate representation of true MMHg enrichment in the SML and its impact on floating objects and the source of aerosol-derived MMHg to marine advective fog and sea spray. Preliminary results of marine aerosol collections will be presented. Establishing and evaluating the pathway of MMHg in the SML would further inform the global cycling of mercury species.

TP-007

RELATIONSHIP BETWEEN MERCURY SPECIES AND MICROBIAL COMMUNITIES IN THE SEAWATER OF THE CENTRAL ADRIATIC SEA

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Natural microbial processes in seawater and sediments can convert inorganic mercury into its toxic form, methylmercury (MeHg). Our research tries to identify relationship between mercury species and microbial abundance in seawater. We performed series of samplings during oceanographic cruises aboard the research vessel Bios Dva from March 2014 to December 2015 in the Central Adriatic Sea. Research was constrained in transect from the Bay of Kastela to the island of Vis. We collected non-filtered water samples for determination of total mercury (THg), dissolved gaseous mercury (DGM), methylmercury (MeHg) and microbial species in Adriatic coastal and open waters. Plankton samples for the determination of THg and MeHg were collected using vertical towing nets (53 and 200 μm). THg concentrations are the lowest in the pristine environment of the island of Vis (0.14-1.10 ng/L). The highest THg values (0.92-5.58 ng/L) are found in the Bay of Kastela which had been affected by previous contamination from chlor-alkali industrial waste waters. DGM always shows slightly higher values in contaminated areas (31.8-351 pg/L) than in the pristine environment (22.1-245 pg/L). MeHg concentrations vary, but range from 1.07-34.3 pg/L for all stations, with the highest values found in the Bay of Kastela. Percentage of THg present as MeHg is low (1.2% and 3.1% in coastal and open sea, respectively) indicating deficiency of conditions for mercury methylation or high MeHg demethylation. MeHg concentration in seawater is correlated with abundance of picoeukaryotes, indicating possible microbial methylation in the water column. Number of picoeukaryotes is the highest in the Bay of Kastela (0.44-31.8 millions/L) which has been affected by industrial effluents from surrounding cities. The lowest number (0.63-19.9 millions/L) is found near the island of Vis. The highest THg concentrations in plankton are found in the Bay of Kastela (49.8-1115 ng/g and 103-249 ng/g d.w. for 53 and 200 μm fraction, respectively), while the lowest values are found at the Split Channel station (39.5-96.5 ng/g and 5.27-96.8 ng/g d.w. for 53 and 200 μm fraction, respectively). MeHg concentrations are more variable (0.29-14.2 ng/g and 2.00-24.3 ng/g d.w. for 53 and 200 μm fraction, respectively). THg concentrations in plankton show biodilution effect which is best seen in the Bay of Kastela. On the contrary, MeHg bioaccumulation along trophic levels is observed through higher MeHg concentrations and MeHg percentage in 200 μm fraction, compared to 53 μm fraction.

1e: Advances in analytical methods for environmental mercury speciation

TP-008

MERCURY SPECIATION AND MASS BALANCES IN CEMENT PRODUCTION PROCESS OF TAIWAN

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Mercury (Hg) is a global pollutant due to its high toxicity, long-distance transport, persistence, and bioaccumulation in the environment, causing adverse effects in human body and animals. The global Hg emissions of anthropogenic sources from cement plants increased from 114 ton in 1990 to 189 ton in 2005 and reached 236 ton in 2010. Cement production has been targeted as the major anthropogenic source of atmospheric Hg, which covers 10% of global Hg emissions. The objective of this study was to understand the Hg mass flows and speciation in two cement plants in Taiwan using the precalciner process. The study results indicated that raw materials, added waste and fuel were the main Hg sources in the cement production process. Hg was mainly emitted in flue gases and present in clinker products. Hg emitted from flue gases was approximately 96.2% for plant 1 and 81.8% for plant 2. The Hg mass balance achieved 96.2% and 85.3% for plant 1 and plant 2, respectively. The Hg enrichment in the kiln and raw mill can be significantly affected by the proportion of Hg recirculated back to the kiln system and that caused high-concentration Hg gas flow emitted from cement plants. The raw mill stack was the main Hg emission source; the total Hg emission concentration was approximately 48.9 g/Nm3 for plant 1 and 23.9 g/Nm3 for plant 2, respectively. Elemental Hg was the major mercury species, followed by oxidized mercury and then particle-bound mercury in the cement process flue gas. The results of this study help gaining a better understanding on Hg emission intensity from the cement production process in Taiwan and provide useful information for developing Hg control strategies in the future.

TP-009

THERMODYNAMIC STABILITY OF MERCURY(II) COMPLEXES WITH LOW MOLECULAR MASS THIOLS STUDIED BY COMPETING LIGAND EXCHANGE AND DENSITY FUNCTIONAL THEORY

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Inorganic divalent mercury (HgII) has a very high affinity for reduced sulfur functional groups. Results from laboratory experiments suggest that HgII complexes with specific low molecular mass (LMM) thiol (RSH) ligands are central for controlling the rate of HgII transformation reactions, in particular the formation of neurotoxic methylmercury (MeHg). Because of methodological limitations for precise determination of the large stability constants of HgII complexes with LMM thiol ligands, constants reported in the literature remain inconsistent. This impedes accurate modelling of the chemical speciation of HgII in natural environments, and to elucidate the importance of HgII complexes with LMM thiols for MeHg formation in natural waters, soils and sediment. Here we report values on thermodynamic stability constants for 15 monodentate, two-coordinated HgII complexes with geochemically relevant LMM thiol ligands, determined by a 2-step ligand exchange procedure. The specific Hg(SR)2 complexes were quantified by liquid chromatography inductively coupled plasma mass spectrometry (LC-ICPMS) using the iodide ion (step 1) or mercaptoacetic acid and 2-mercaptopropionic acid as competing ligands. Determined thermodynamic constants (log 2) for the investigated Hg(SR)2 complexes ranged from 34.6, N-Cysteinylglycine, to 42.1, 3-mercaptopropionic acid, for the general reaction Hg2+ + 2RS- = Hg(SR)2, where RS- represents the thiolate group containing compound. Density functional theory calculations showed that HgIILMM thiol complexes are stabilized by electron-donating carboxyl and carbonyl groups, and destabilized by electron-withdrawing protonated primary amino groups. Experimental and modeling results demonstrated significant differences in the stability of Hg(SR)2 complexes, depending on the presence of the electron withdrawing or donating functional groups in the vicinity of the RSH group. These differences in stability are expected to largely effect the chemical speciation of HgII and its transformation reactions in environmental systems.

TP-011

A NEW SIMPLIFIED EXTRACTION METHOD FOR THE DETERMINATION OF MEHG IN SEAFOOD BY LC-UV-CV-AFS.

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Methylmercury is the most toxic mercury species to humans. The main source of this species in our diets comes from seafood. It is therefore of high importance to monitor the concentration of MeHg in food of marine origin. Here, a simple extraction for MeHg in seafood is detailed. The method uses an extraction with 10mM APDC in 80% MeOH at 60oC, followed by ultrasonication. The mercury speciesare subsequently separated with RP-LC using 1.5mM APDC in 80% MeOH as a mobile phase. The eluting Hg species are then on-linechemicallyoxidisedand reduced with acidified Br-/BrO3- and SnCl2before AFS detection. This method of extraction has been tested using various marine CRMs with a moisture correction applied in each case. A higher concentration of APDC for extraction gave a yield much closer to the specified value,and also amuch smaller standard deviationcompared toan APDC concentration closer to that of the mobile phase. The results of all CRM measurements showed little to no loss of MeHg when compared to the specified concentrations.Recovery values rangedfrom 92.7% to 103.7%. The data also showed high precision, indicated by the low standard deviations obtained, which ranged from 0.3% to 5.1%.

TP-015

IDENTIFICATION OF MERCURY AND DISSOLVED ORGANIC MATTER COMPLEXES USING ULTRA-HIGH RESOLUTION MASS SPECTROMETRY

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The chemical speciation and bioavailability of mercury (Hg) is markedly influenced by its complexation with naturally dissolved organic matter (DOM) in aquatic environments. To date, however, analytical methodologies capable of identifying such complexes are scarce. Here we utilize ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) coupled with electrospray ionization to identify individual Hg-DOM complexes. The measurements were performed by direct infusion of DOM in 1:1 methanol:water solution at a Hg to dissolved organic carbon (DOC) molar ratio of 3×10-4. Heteroatomic molecules, especially those containing multiple S and N atoms, were found to be among the most important in forming strong complexes with Hg. Major Hg-DOM complexes of $C_{10}H_{21}N_2S_4Hg^+$ and $C_8H_{17}N_2S_4Hg^+$ were identified based on both the exact molecular mass and patterns of Hg stable isotope distributions detected by FTICR-MS. Density functional theory was used to predict the solution-phase structures of candidate molecules. These findings represent the first step to unambiguously identify specific DOM molecules in Hg binding, although future studies are warranted to further optimize and validate the methodology so as to explore detailed molecular compositions and structures of Hg-DOM complexes that affect biological uptake and transformation of Hg in the environment.

TP-016

EFFECT OF ORGANIC MATTER ON MERCURY PARTITIONING IN SOIL: APPLICATION OF DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE

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In this study, we used the diffusive gradients in thin films (DGT) to understand how soil properties (i.e., organic matter content) affect partitioning behaviors of Hg between soil particles and pore water. The accumulated mass of Hg in DGT gel and soil pore water was monitored for 10 days, while Hg concentration changed from 1 to 50 ppm and soil peat moss content from 5% to 20%. Using these experimental data, we were able to estimate Tc (response time) and Kd (distribution coefficient between soil and pore water) as a kinetic and equilibrium parameter, respectively, of Hg using the DGT induced fluxes in sediments and soils (DIFS) model, and k1 (DGT uptake rate constant) and k2 (DGT elimination rate constant) using the one compartment model (OCM). When Hg concentration in soil increased from 1 to 50 ppm, Tc decreased from 146 to 1 (s) and Kd increased from 18 to 107 cm3 g-1. Using the same data, the OCM predicted that k1 decreased from 2.6 x 10-6 to 5.8 x 10-7 kg soil cm-2 d-1 and k2 increased from 3.1 x 10-2 to 2.0 x 10-1 d-1 along with increases in Hg concentration. When the soil peat moss content increased from 5 to 20%, Tc increased from 338 to 1000 (s), and Kd decreased from 82 to 1.5 cm3 g-1. Using the same experimental data, the OCM predicted that k1 decreased from 1.2 x 10-5 to 4.0 x 10-6 kg soil cm-2 d-1, and k2 increased from 0.21 to 1.1 d-1 while peat moss content increased. These results indicate that the mobilization rate of Hg from soil to DGT, indicated by Kd and k1, tends to decrease with increasing organic matter content, which could be a result of the strong binding of Hg to the soil organic matter. In addition, pore water depletion of Hg was quantified as a function of distance from the DGT interface and deployment time. These results also showed that high organic content in soil increase the depletion of Hg in pore water. The combined approaches of DGT, DIFS and OCM allow us to obtain better understanding on the partitioning of Hg involved in soil retention and mobilization, suggesting that these are suitable tools to predict metal bioavailability in soils.

TP-017

IMPROVEMENTS TO THE COLLECTION OF ATMOSPHERIC MERCURY SPECIES

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The Tekran Atmospheric Mercury Speciation system is the only commercially available instrumentation capable of measuring mercury species semi-real time producing high resolution data required to identify local point sources. Recently problems with Gaseous Oxidized Mercury capture efficiency and retention have been identified and several groups are working on improving these measurements.

In September, 2015, the National Oceanic and Atmospheric Administration and the National Atmospheric Deposition Program (NADP) organized a Tekran User Group Meeting in Washington DC. The group discussed these speciation collection problems and improvements to measurement methodology. Experimental tasks were assigned to groups to test ideas for improving the speciation measurements. This poster will examine these experimental results and identify potential modifications to the NADP Atmospheric Mercury Network (AMNet) Standard Operating Procedures. Additionally, this poster will give Tekran users the opportunity to discuss these changes with the AMNet Site Liaison.

TP-018

MERCURY SPECIATION IN SEABIRD FEATHERS USING SPECIES-SPECIFIC ISOTOPE DILUTION ANALYSIS BY GC-ICPMS

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Mercury (Hg) toxicity is known to be strongly dependent on its speciation, being monomethylmercury (MeHg) the most dangerous species since it is bioaccumulative in food webs. Seabirds are considered as effective sentinels of environmental marine contamination and their feathers are extensively used as non-lethal samples for contaminant biomonitoring. This tissue represents the main route for Hg elimination in seabirds and contains predominantly MeHg. However, measuring both MeHg and inorganic Hg (iHg) in feather samples is necessary to better evaluate the impact of Hg in seabirds and understand their

metabolic response. In addition, it has been documented that historical feather collections could experience a contamination with iHg associated to museum preservatives, consequently Hg speciation analyses are required in these cases. In this work, we developed a robust analytical technique for precise and accurate simultaneous quantification of MeHg and iHg in feathers by gas-chromatography (GC)-ICPMS analyses using double species-specific isotope dilution technique (D-IDA). An optimisation of the extraction method was carried out by testing different extraction systems, reagents and spiking procedures in an internal reference feather sample (composed of a pool of feathers of king penguins). The procedure was validated with a human hair certified reference material (NIES-13). Microwave nitric acid extraction with spike addition before the extraction provided the best recoveries relative to certified NIES-13 values (96.0±1.2% for MeHg and 95.9±0.2% for THg) and was then chosen as the most appropiate extraction method. Our developed method was applied to feather samples from a large number of seabird species from the Southern Ocean (Antarctic prions, petrels, albatrosses, penguins and skuas) to investigate the variability of Hg speciation across a large range of diet, areas and therefore of Hg exposure conditions and concentrations.

TP-019

LABILE AND STABLE FORMS OF MERCURY IN SOIL AND SEDIMENT SAMPLES – DEVELOPMENT OF A THERMO-DESORPTION METHOD FOR HG FRACTIONATION

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Mercury transformation and transport in the environment strongly depend on its chemical form. Information about Hg form is also important for understanding the bioavailability as well as toxicity of this element. There are many methods for Hg speciation but most of them are expensive and time consuming. Therefor none of them is used in routine analysis. The aim of this research was to develop and validate a simple thermo-desorption technique for mercury fractionation in soil and sediment samples using commercially available mercury analyzer.

The direct mercury analyzer DMA-80 (Milestone, Italy) was used for the detection of Hg. For temperature fractionation the same instrument was used, only the temperature of catalytic tube heating was changed. In this case the temperature at which Hg was released from the samples was controlled. Each sample was heated from 50 to 750 degrees Celsius and result was presented as a thermo-desorption curve. The Hg species were characterized by the temperature range at which they were release. Fourteen synthetic standard material were used in this work. Additionally, the natural standards: humus-like substance and MeHg standard were used. The method was tested on a certified reference material (INCT-TL-1; NCS DC 87103; BCR-414) as well as on natural samples: soil, beach sand and marine sediment.

The obtained results show that the four-step thermo-desorption method can be considered as a fast and reliable screening technique for the evaluation of the percentage contribution of certain groups of Hg compounds with similar properties in solid samples with low, environmental Hg concentration. The developed method allows for separation of Hg fraction associated with labile compounds such as: mercury halides, mercury perchlorate, mercury nitrate, mercury cyanide, mercury thiocyanate,mercury fulminate,mercury acetate,methyl mercury and humus-like substance (labile-1); mercury sulfate, mercury oxide (red) andmercury fluoride (labile-2) as well as with mercury sulphide (stabile-1) and mineral matrix (stabile-2). The method was tested in the range of Hg concentrationfrom 2.4 to 262.5 ng/g d.w. Good repeatability and accuracy of the results were obtained. The developed method is less expensive than alternative methods for Hg fractionation, because it does not require the use of reagents. It also limits the possibility of contamination of the sample. The method was introduced on commercially available mercury analyzer without additional software modifications. This will allow for standardization of operational conditions. This makes the method can be widely used in laboratories engaged in biogeochemical transformations of mercury in the environment.

TP-020

DEVELOPMENT OF NANOGOLD-MODIFIED DIPSTICKS FOR QUICK AND REAGENT-FREE MERCURY DETERMINATION IN WATER SAMPLES

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In this work several approaches for the preparation of nanogold-modified accumulation chips (dipsticks) are presented. Due to its chemical inertness and its thermal stability quartz glass slides were used as a substrate. In a first step, the surface of the substrate was coated with a thin gold film by vapor plating. By use of an annealing process, the smooth gold film was nano-structured. Investigation by atomic force microscopy confirmed successful formation of gold islands or rods in the nano-scale and a significant increase in the surface roughness of the carrier. Furthermore, AFM images show that the size of the nanogold particles could easily be regulated by variation of temperature and heating time. In order to prove the feasibility of the prepared dipsticks for mercury accumulation, several experiments in Hg(II) aqueous solutions were performed. After accumulation, Hg was released from the dipstick by thermal desorption and measured by atomic fluorescence spectrometry. A successful calibration experiment in the ng L-1 range evidences a linear increase in the fluorescence intensity with higher Hg concentrations. The limit of detection (LOD) was found to be as low as 0.18 ng Hg L-1 and a high reproducibility with a relative method standard deviation of 7.3 % (n=12) is given. Time-dependent accumulation experiments show a linear correlation between the mercury accumulation rate and the exposure time of the dipstick in the aqueous Hg(II) solution. However, in order to enhance the accumulation rate, in a second approach dipsticks with higher load of small gold nanoparticles should be prepared. Therefore, the glass surface was first functionalized using 3-aminopropyltrimethoxysilane (APTMS). Then, silica nanoparticles with a diameter of approx. 300 nm were immobilized on the surface to enlarge the surface area. After a second APTMS coating a thin gold film (10 nm thickness) was deposited on the surface by vapor plating. By use of an annealing process, the smooth gold film was transformed into nanoparticles. The successful formation of gold nanoparticles and their homogeneous distribution on the surface was proved by scanning electrode microscopy images, revealing an average particle diameter of 31.4 15.3 nm (N=364) after thermal treatment. Here again, mercury accumulation was tested in several exposition experiments in aqueous model solutions.

TP-021

DETERMINATION OF ATMOSPHERIC ELEMENTAL MERCURY OVER METROPOLITAN TAIPEI, TAIWAN BY AN AUTOMATED GASEOUS MERCURY ANALYZER

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A novel Automated Gaseous Mercury Analyzer (AGMA) was custom-made to fully investigate the gaseous elemental mercury (GEM) in the overlying air of Taipei, Taiwan. The design principle is based on hyphenation technique by flow injection-Au amalgamation analysis with cold vapor atomic fluorescence detector. This analyzer gained several advantages in terms of simplicity, efficiency, precision, accuracy and versatility. The characteristic feature of the AGMA is firstly a computer-assisted dual-channel detection device so that continuous measurements can be simultaneously performed in two separate channel lines for Hg sampling and analysis. The automated system effectively increases the sample throughput and analytical performance of the GEM in environmental ultra-trace levels. The AGMA is also well suitably employed in the general laboratory or other field stations (e.g., shipboard use) with any risk of ambient contamination to obtain the high-quality Hg data in different environmental airs. In a field test in Taipei, we observed the diurnal GEM variation with higher levels in the noon and lower in the mid-night, similar to those in the ozone, PM10, PM2.5, solar irradiance. The observed diel pattern was closely related to local human activities, solar irradiance and surface air temperature in metropolitan Taipei.A novel Automated Gaseous Mercury Analyzer (AGMA) was custom-made to fully investigate the gaseous elemental mercury (GEM) in the overlying air of Taipei, Taiwan. The design principle is based on hyphenation technique by flow injection-Au amalgamation analysis with cold vapor atomic fluorescence detector. This analyzer gained several advantages in terms of simplicity, efficiency, precision, accuracy and versatility. The characteristic feature of the AGMA is firstly a computer-assisted dual-channel detection device so that continuous measurements can be simultaneously performed in two separate channel lines for Hg sampling and analysis. The automated system effectively increases the sample throughput and analytical performance of the GEM in environmental ultra-trace levels. The AGMA is also well suitably employed in the general laboratory or other field stations (e.g., shipboard use) with any risk of ambient contamination to obtain the high-quality Hg data in different environmental airs. In a field test in Taipei, we observed the diurnal GEM variation with higher levels in the noon and lower in the mid-night, similar to those in the ozone, PM10, PM2.5, solar irradiance. The observed diel pattern was closely related to local human activities, solar irradiance and surface air temperature in metropolitan Taipei.

1f: Quantifying mercury emissions from energy generation

TP-023

THE INFLUENCE OF HIGH H2O ON MERCURY OXIDIZATION IN SIMULATED HOMOGENEOUS OXY-COMBUSTION ATMOSPHERE

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The key point in the research of mercury emission control from new coal combustion type, such as coal oxy-combustion (O2/CO2), is full knowing of mercury speciation emission from coal combustion in homogeneous O2/CO2 atmosphere, especially definite understanding of the influence of high H2O concentration on mercury oxidization in homogeneous O2/CO2 atmosphere. Based on the established bench-scale experimental apparatus, it studied the influence of high H2O concentration on mercury oxidation in the simulated flue gas of homogeneous O2/CO2 atmosphere. The results showed that the high H2O concentration in simulated O2/CO2 atmosphere inhibited the oxidization of mercury through three ways. The high H2O concentration not only inhibited the generation of oxidizing Cl but enhanced the consumption of oxidizing Cl, and it inhibited directly the mercury oxidization in the simulated flue gas of homogeneous O2/CO2 atmosphere. The oxidation rate of elemental mercury (Hg0) with the addition of 5% water was smaller average 30% than that without additional water. The existence or addition of SO2 also inhibited the transformation of Hg0 to Hg2+. SO2 enhanced the consumption of oxidizing Cl to inhibit the mercury oxidization. Conversely, the inhibitory effect of high H2O on mercury oxidization was overcame at the extent by the addition of HCl in the simulated flue gas of homogeneous O2/CO2 atmosphere. The high HCl concentration promoted the conversion of HCl to oxidizing Cl to improve the mercury oxidization at last.

TP-024

NEW APPROACH TO DYNAMIC RANGE ENLARGEMENT IN MERCURY ANALYSIS OF SORBENT TRAPS

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Sorbent trap monitoring systems have been successfully used in the USA to measure mercury at low levels mandated by the MATS (Mercury and Air Toxics Standards) and the NESHAP (National Emission Standards for Hazardous Air Pollutants). The mass of mercury collected on sorbent traps can vary in range across six orders of magnitude, depending on the Hg concentration in stack gas and sampling duration. During several days of sampling stack gas according to the monitoring procedure prescribed by EPA Performance Specification 12B, the collected mass of mercury may reach hundreds of micrograms. Most often, the sorbent traps are analyzed via atomic absorption spectroscopy (AAS) using a thermal technique (desorption or combustion), which does not require any chemical treatment. However, there is a risk to lose the analytical data if the mass of collected mercury exceeds the calibration range of the analytical instrument. Often while working with conventional gold-trap analyzers, the sample is homogenized and divided into several independently analyzed subsamples to avoid saturation of the analytical signal. Such an approach increases measurement error.

Here we present a novel approach to sorbent trap analysis which eliminates the risk of losing data while analyzing samples with unknown amounts of accumulated mercury. The technique is based on the commercially available Zeeman atomic absorption analyzer RA-915M. Direct analysis without intermediate mercury pre-concentration on a gold trap enables automated real-time control of the atomizer heating based on dynamics of the mercury released from a sample. Accumulated laboratory experience of sorbent trap analysis across a range of 1 1,000,000 ng Hg has shown excellent reliability of this rapid method for routine analysis of sorbent traps and other samples with unknown Hg content.

TP-025

MERCURY (II) REDUCTION AND SULFITE OXIDATION IN FLUE GAS DESULFURIZATION WASTEWATER: KINETIC STUDY AND SPECIATION MODELING

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The re-emission of mercury (Hg), as a consequence of the formation and dissociation of the unstable complex HgSO3, is a problem encountered in flue gas desulphurization (FGD) treatment in coal-fired power plants. A model following a pseudo-second-order rate law for Hg2+ reduction was derived as a function of [SO3 2-], [H+] and temperature and fitted with experimentally obtained data to generate kinetic rate values of (0.120 ± 0.04, 0.847 ± 0.07, 1.35 ± 0.4) mM-1 for 40°, 60°, and 75°C, respectively. The reduction of Hg2+ increases with a temperature increase but shows an inverse relationship with proton concentration. Plotting the model-fitted kinetic rate constants yields ΔH = 61.7 ± 1.82 kJ mol-1, which is in good agreement with literature values for the formation of Hg0 by SO32. The model could be used to better understand the overall Hg2+ re-emission by SO32- happening in aquatic systems such as FGD wastewaters.

TP-012

STABILISATION/FIXATION FOR DISCHARGING NON TOXIC MERCURY COMPOUNDS (HGS) FROM SCRUBBER SYSTEMS OF HAZARDOUS/MUNICIPAL WASTE INCINERATIONS (WCI) PLANTS AND FGD POWER STATIONS

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In every thermal combustion plant you can measure and detect mercury from the scrubber through the flue gas to the chimney up to the environment. As a standard treatment, activated carbon/coke is used to adsorb the mercury. The loaded adsorbent is disposed on a landfill. In terms of gas limit values, this system works well. But not for a sustainable, holistic treatment. Mercury leach out and forms by microbiology, organic mercury. Mercury becomes even more toxic. For this reason, mercury must be removed as insoluble HgS from this cycle. HgS is a natural mineral, called cinnabar. The only non-toxic mercury compound. Scrubber systems have an opportunity to buffer and store mercury salts (e.g. HgCl2/HgCl4) in high saturation. Under normal conditions the systems are running stable, with no risk of Hg0-gas blow out. But the concentration of dissolved mercury is the magnitude of influence for a Hg0-blow out event. Of course in an event of high input of reducing agent (e.g.SO2), the ionic(dissolved)Hg compounds transformed to elemental Hg. In this case a Hg-gas blow out is happened. In case of a mercury event, the mercury breaks through the scrubber and contaminates the subsequent purification stages. Hg deposits can be bleed out all the time and generate a baseline of Hg-emission, only a few g below the current limits. But the environment is continuously contaminated and poisoned with tons of Hg/year. The use of a special inorganic polymeric sulfur compound in an acidic scrubber or FGD plant produces only insoluble non-toxic HgS. HgS is chemically and thermally very stable. Therefore, HgS can be treated both in a classic sewage treatment and in a spray dryer. Here is the only point for Hg, where its allowed to leave the plant. Only as HgS. With this technology, it is made impossible to form an internal dissolved Hg cycle in the scrubber system. Unexpected events can be buffered. There are no Hg-blow outs possible. This is an effective way to separate mercury from a scrubber system. The special inorganic polymeric sulfur liquid (NETfloc SMF1) is easy to dose into any scrubber systems. Regular analyzes of the mercury balance (Hg dissolved/Hg insoluble) in the scrubber help to determine the optimum dosing level also for best cost efficiency. The German Umwelt Bundesamt (UBA) has tested HgS as the best choice for deposition of mercury compound in underground dumps.

TP-013

ALTERNATIVE THERMAL DESORPTION HG ANALYSIS WITH NEW BROMINE-SORBENT TRAP AND RECONSIDERATION OF IODINE-SORBENT AND ITS ANALYTICAL BIAS ISSUES

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The sorbent trap method (STM) is popularly used for Hg sampling and monitoring from coal power plant.

US EPA Method 30B is reference method for RATA (Relative Accuracy Test Audit) test for Hg CEM and sorbent trap monitoring system, and short-term snapshot of Hg emission. PS-12B is for long-term Hg monitoring method up to 10 days sampling.

Iodine treated activated carbons (I-ACs) is mostly employed for STM, but iodine causes matrix interference for wet analysis as well as it can be easily decomposed to iodine vapors (I2) for thermal analysis that results in quick destruction of catalyst/gold amalgam, which restricts various applications of Hg analysis device and method for STM.

The iodine contaminated Hg analyzer may lead analytical bias issues such as discrepancy of elemental Hg spiked and liquid Hg standard sample, low recovery of Hg, and poor calibration, which result in invalidation of field sampling and significant failure of QA/QC criteria.

Newly developed brominated ACs (Br-ACs) sorbent media showed enough Hg adsorption capacity as much as I-ACs and observed good thermal stability at desorption analysis temperature (650 oC).

In this study, a successful calibration could be achieved with the alternative thermal desorption Hg analysis system by using new Br-ACs.

The new Br-ACs sorbent can be consider as a replacement of I-ACs, which allows various type of Hg analysis devices (either catalyst or non-catalyst type) and analysis methods (e.g. acid digestion) for STM.

1h: The role of global monitoring in evaluating regulatory effectiveness

TP-027

MERCURY AND OTHER TREND MONITORING OF GREAT SLAVE LAKE UNDER CHANGING CLIMATE AND GLOBAL EMISSIONS

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Under the Northern Contaminants Program, we are investigating mercury (Hg) in Great Slave Lake (GSL) which is located in Canada's Northwest Territories. While North American Hg emissions have decreased, Asian emissions are increasing with their expanding economies. Climate change, including warming trends, may enhance productivity resulting in more fish prey and increased Hg methylation rates. Hg concentrations in food webs may increase in top piscivores although this may be counteracted by growth dilution.

Our study focuses on Lake Trout (Salvelinus namaycush), a cold-water pelagic species and Burbot (Lota lota), a cool-water benthic species. Both are omnivores, consuming invertebrate prey in addition to fish. Since 1998, Burbot and Lake Trout have been provided annually from East Arm (EA) by Lutsel K'e and the West Basin (WB) by Fort Resolution and Hay River with earlier mercury records available. The EA is cold, deep and oligotrophic; the WB is shallower, warmer, and more productive, largely due to the Slave River, a substantial source of water, suspended sediments, organic matter and plant nutrients.

Over 1993-2016, EA Lake Trout were slightly smaller (600±69 vs. 634±76 mm) than WB fish but older (15.5±4.8 vs. 9.7±4.0 yr) indicating lower growth rates; Hg concentrations were lower (0.17±0.08 vs. 0.20±0.08 µg/g) possibly because of a less fish-rich diet and/or lower Hg inputs and methylation rates in the EA than WB. WB Lake Trout Hg concentrations increased from the late 1970s to 2016. In the EA, Hg concentrations decreased in small (495-600 mm) fish but increased in large (600-800 mm) fish. The presence of many old fish (>20 yr), with different growth rates, presents challenges in trend analyses, particularly in the EA.

EA Burbot were smaller (539±62 vs. 663±74 mm), younger (10.4±2.4 vs. 13.0±3.2 yr) and with lower Hg concentrations (0.14±0.06 vs 0.16±0.07 µg/g) than WB fish. Hg concentrations increased over 1995-2016 in both regions.

Distinct warming trends in air temperatures have occurred over the past century; sedimentation rates and algal carbon concentrations have increased and diatom assemblages have changed; there is less evidence of recent increases in Hg concentrations and sediment flux. Trends of Hg increase in Lake Trout and Burbot were more strongly related to cooler years than warming trends. There was little evidence of changes in trophic feeding over the period of record. With low Hg concentrations, GSL continues to be an important source of fish to northerners.

TP-029

GASEOUS ELEMENTAL MERCURY OBSERVATIONS OVER THE SOUTHERN OCEAN FROM THE CAPE GRIM BASELINE AIR POLLUTION STATION

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The southern hemisphere (SH) and in particular Australia are not well represented, in contrast to the northern hemisphere, in terms of long time series of atmospheric mercury measurements. Recent studies have highlighted that the mean background of gaseous elemental mercury (GEM) for the SH is substantially lower than previously thought (i.e., based on spare data). The Cape Grim Baseline Air Pollution Station (CGBAPS), a Global Atmospheric Watch (GAW) station, is situated on the north-west peninsula of Tasmania, Australia (40.68° S, 144.68° E). GEM measurements have been undertaken at CGBAPS since September 2011. This location and the predominantly westerly winds in the region give CGBAPS access to air masses that have equilibrated with the Southern Ocean. Radon measurements at the site were used to determine air masses of oceanic fetch. For other wind sectors air masses are influenced by terrestrial surfaces. The six year time series from the Cape Grim station has been evaluated to determine mean background as a function of wind sector, as well as seasonal and inter-annual trends. An overall background GEM concentration at Cape Grim of 0.85 ng m-3 was determined with very little inter-annual variability with low seasonality.

TP-030

FOUR YEARS (2011-2015) OF TOTAL GASEOUS MERCURY AND OTHER KEY MEASUREMENTS FROM THE CAPE VERDE ATMOSPHERIC OBSERVATORY (CVAO)

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Here we will report four years (Dec 2011 – Dec 2015) of Total Gaseous Mercury (TGM) measurements at the Cape Verde Observatory (CVO), a global WMO-GAW station located in the sub-tropical remote marine boundary layer (16.85°N, 24.87°W). The measurements presented here are part of the EU Global Mercury Observation System (GMOS) network. The GMOS network of sites was established in 2011 with the aim of addressing known gaps in the spatial and temporal measurement of mercury, as well as improving knowledge of Hg speciation.

Observed TGM concentrations were between 1.03 and 1.33 ng m-3 (10th, 90th percentiles), close to the expectations based on previous interhemispheric gradient measurements. We observe a decreasing trend in TGM (0.04 ± 0.03 ng m-3 yr-1, -3.4% ± 2.4% yr-1) over the four years consistent with the reported decrease of mercury concentrations in North Atlantic surface waters and reductions in anthropogenic emissions. The trend was more visible in the summer (Jul-Sep) than in the winter (Dec-Feb), when measurements were impacted by air from the African continent and Sahara/Sahel regions. These African air masses were also associated with the highest and most variable TGM concentrations. We attribute the smaller decreasing trend to the influence of large anthropogenic sources in West Africa such as from artisanal and small-scale gold mining (ASGM).

In addition to the TGM measurements, we will show time series and interpretation of other climatically significant trace gases and greenhouse gases, for which we have up to ten year records from the Observatory. We will discuss the importance of these measurements and outline some of the plans for the future of the CVAO.

TP-031

ONGOING MONITORING OF FOREST SOIL MERCURY IN VERMONT, USA

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Continued monitoring of total mercury (THg) concentration in soils is essential for detecting, predicting and addressing environmental change. In cooperation with the Vermont Monitoring Cooperative (now the Forest Ecosystem Monitoring Cooperative), we have established a long-term soil monitoring study in forested sites in the northeastern USA where annual wet deposition of Hg has been in the range of 6-10 µg/m2. Five 50 x 50 m plots were located in protected areas, three on Mt. Mansfield in north-central Vermont and two in the Lye Brook Wilderness Area in southwestern Vermont. Elevation ranges from 590 to 1140 m with forest type changing from typical northern hardwood (Acer saccharum, Betula alleghaniensis and Fagus grandifolia) to high-elevation spruce-fir (Picea rubens and Abies balsamea). Each plot contains 100 5 x 5 m subplots with sampling date assigned randomly (10 per date). The initial sampling of these plots took place in the summer of 2002 and resampling occurred in 2007 and 2012. Small pits were dug in the center of each plot and the soils were sampled both by genetic horizon and depth increments. These samples have been analyzed for a suite of chemical parameters, including exchangeable cations, carbon and nitrogen. Separate samples of the uppermost humified horizon (Oa or A) were taken for total Hg (THg) analysis using appropriate protocols. Average THg concentration at each site ranged from ~200-500 ng/g. The average carbon concentration in these horizons varied between ~100-420 g/kg. There was a positive elevational gradient of THg concentration, consistent with greater deposition and with other studies. The THg:C ratio (ng/g) ranged from 0.6-1.8, with the highest ratio at the highest elevation. Continued sampling at 5-year intervals will allow detection of environmental change in response to both a changing climate and changing Hg deposition.

2a: Sources and cycling of mercury in coastal ecosystems

TP-033

MERCURY BIOACCUMULATION IN THE NORTHERN MARINE FOOD WEB OF EAST HUDSON BAY, CANADA: PRELIMINARY RESULTS

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Communities in east Hudson Bay and James Bay (Canada) are concerned about ecosystem changes observed in recent decades, particularly related to sea-ice and oceanographic conditions, and also about potential impacts of contaminants from long-range atmospheric transport and regional human activities. The Arctic Eider Societys Community-Driven Research Network (CDRN) has been established to measure and better understand large-scale cumulative environmental impacts in that marine region. Building on CDRN collaborations and activities in five communities (Sanikiluaq, Kuujjuaraapik, Inukjuak, Umiujaq, Chisasibi), this project funded by the Northern Contaminants Program is generating new information on metal bioaccumulation that will provide a regionally-integrated perspective on metal exposure in the marine environment. The five communities are sampling coastal bioindicator species (blue mussel, common eider) annually for three years (2015 to 2017). Offshore bioindicators (ringed seal, herring gull, plankton, fish) are additionally being collected from two of the communtiies. These locally-important bioindicators of metal accumulation will be used to characterize geographic and habitat-specific variation (coastal and offshore zones) in east Hudson Bay and James Bay. This poster will present preliminary results from collections in 2015 and 2016 of herring gull eggs, ringed seals, blue mussels, and common eiders. Animal tissues were analyzed for total mercury, methylmercury (on a subset of samples), 24 elements by ICP-MS, and carbon and nitrogen stable isotopes. Spatial variation of tissue mercury concentrations in east Hudson Bay and James Bay will be examined. Food web structure has been characterized using carbon and nitrogen stable isotope ratios, and trophic position and carbon source were found to affect mercury bioaccumulation. Higher mercury levels in blue mussels were associated with bioaccumulation of terrigenous and redox-sensitive elements (e.g., barium, uranium, vanadium, iron, manganese), suggesting that large river inputs may affect mercury bioaccumulation near the base of the food chain in coastal environments. This three-year project will generate important baseline information on mercury levels in the food web to allow for future tracking of impacts from environmental change, long-range atmospheric transport, and regional human activities on this arctic marine ecosystem.

TP-034

MERCURY BIOGEOCHEMICAL CYCLE IN A SUBTROPICAL MANGROVE

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The purpose of this study was to investigate the input and distribution of total mercury (Hg) in the leaf litter fraction and its importance to the sediment of mangrove using the elemental and isotopic composition of carbon and nitrogen to characterize the organic matter in the estuarine area of the Paraíba do Sul river, Southern Brazil. The average concentrations of Hg in sediment were 81 ± 32 ng.g-1 Site 1 (Laguncularia racemosa), 62 ± 15 ng.g-1 Site 2 (Rhizophora mangle) and 110 ± 16 ng.g-1 Site 3 (Avicennia germinans). The carbon isotopic composition (δ13C) in the sediment ranged from -29.40 to -26.49 ‰ and nitrogen (δ15N) from 2.38 to 5.83 ‰. The Hg concentration in annual litter fall were: 21 ± 2 ng.g-1;16 ± 4 µg/m2/ano; 18 ± 1 ng/g-1; 17 ± 3 µg/m2/ano-1; 53 ± 4 ng.g-1; 33 ± 4 µg/m2/ano for Laguncularia racemosa, Rizophora mangle and Avicennia germinans, respectively. The isotopic composition in the litter varied from -28.59 to -26.91 ‰ for δ13C and 4.48 to 7.21 ‰ for δ15N. The elemental and isotopic data in the sediment reflected the values of the dominant plant species at each sampling site. The results show that the dominant species (A. germinans) stands for higher Hg values in the sediments as well as the input for this element via litter. Since Hg in mangrove sediment has a low mobility, our results are suggesting that the atmosphere deposition has been playing an important role in Hg biogeochemical cycle in mangrove ecosystems through atmospheric deposition under the canopy. The Hg input data obtained from the litter, although lower compared to the closest point sources of contamination areas, fall into the mangrove ecosystem as an important integrator for Hg in the air, vegetation and sediment.

TP-035

EVALUATING THE INFLUENCE OF CELL SIZE AND SALINITY GRADIENTS ON MERCURY UPTAKE BY PHYTOPLANKTON IN COASTAL LAGOON ECOSYSTEMS

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Phytoplankton are the typical entry point for mercury in marine food webs, and subsequent mercury bioaccumulation in fish is the principal route of human exposure. Although primary producers form this critical link, the biological and physical factors that influence mercury uptake by phytoplankton are not well understood, particularly in coastal lagoons where our previous work suggests elevated monomethylmercury (MeHg) production relative to coastal seawater. We are combining laboratory and in situ field incubation experiments to determine how cell size and salinity gradients affect mercury bioaccumulation in cultured diatoms (T. weissflogii and T. oceanica), and in natural phytoplankton populations. T. weissflogii (~17 µm length; ~11 µm width) and T. oceanica (~6.5 µm length; ~5 µm width) are centric diatoms with a consistent disk shape that allows comparison of their surface area to volume ratios. Lab cultures of these diatoms were acclimated to a salinity range of 10 to 30 to simulate fresh water and seawater mixing at the land-sea margin. These cultures were grown in ~10 and ~100 pM MeHg, in addition to non-spike controls, to assess the effects of cell size and salinity on MeHg uptake. The companion field incubation experiment was conducted at San Elijo Lagoon in Southern California. Lagoon water was filtered through a 200 µm mesh screen to eliminate zooplankton grazers, then poured into clear polycarbonate carboys and spiked to MeHg concentrations of ~10 and ~100 pM, in addition to no-spike controls. The carboys were incubated in the lagoon for 12 to 36 hours prior to filtration. Chlorophyll-a concentrations indicate that at the time of our study, the phytoplankton community was comprised of 15% picoplankton (0.2-2 µm), 55% nanoplankton (2-20 µm) and 30 % microplankton (20-200 µm). Over the first 24 hours of the incubation, chlorophyll-a in the carboys increased from approximately 6 µg/L to 10 µg/L, while nutrient concentrations decreased, suggesting the absence of grazers enabled a small phytoplankton bloom. This comparison of total mercury and MeHg among various phytoplankton communities will help us understand the drivers of mercury uptake in these understudied coastal lagoon ecosystems.

TP-036

SEASONAL DRIVERS OF MERCURY UPTAKE BY PHYTOPLANKTON IN A SOUTHERN CALIFORNIA COASTAL LAGOON SYSTEM

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California's coastal lagoons provide essential habitat for threatened and endangered species, yet eutrophication causes many lagoons to experience multiple algal blooms each year that could affect mercury (Hg) bioaccumulation in marine food webs. Specifically, anoxia associated with eutrophication favors monomethylmercury (CH3Hg+ or MeHg) production, and phytoplankton blooms provide a mechanism for MeHg entry into the food web. Because coastal lagoons are highly dynamic, we are evaluating both short-term (e.g., tidal) and long-term (e.g., seasonal) trends in mercury cycling. We conducted bimonthly sampling to measure chlorophyll-a, particulate organic carbon, and phytoplankton cell size (flow cytometry), along with the concentration of total Hg and MeHg in filtered (< 0.2 µm) and unfiltered water at San Elijo Lagoon in Southern California. Potential sources and transport mechanisms of MeHg were also evaluated by sampling shallow (< 3 m) groundwater and nearshore seawater at the lagoon mouth. Monitoring data show that dissolved oxygen in San Elijo Lagoon often fluctuates between > 100% (high tide) and < 30% (low tide), possibly due to the discharge of anoxic groundwater, which may be an important source of MeHg. This system also experiences extreme seasonal changes which are, in part, driven by the opening and closing of a sand berm at the lagoon mouth. When the berm is open, the lagoon is in direct exchange with the ocean (i.e., estuarine conditions). During closed conditions, drainage from the watershed remains trapped behind the sand berm and the lagoon becomes eutrophic (multiple blooms with chlorophyll-a > 10 µg/L). Additionally, long periods of drought can induce reverse estuarine conditions, in which seawater entering the lagoon during high tide becomes warmer and more saline than coastal seawater as a result of evaporation and a lack of freshwater inputs. The semi-enclosed geomorphology of coastal lagoons, combined with the occurrence of frequent algal blooms, provide an ideal setting to study the biological and physical drivers of mercury uptake by phytoplankton.

TP-037

MODELLING THE CHANGING MERCURY CYCLING AND BIO-ACCUMULATION IN THE NORTH- AND BALTIC SEA OVER THE LAST 60 YEARS

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The toxicity of methyl mercury was first discovered after the 1950ties Minamata incident in Japan. Since then, it was found that methyl mercury is a non-threshold pollutant that impairs the development of the human brain. One of the main sources for mercury intoxication is the prenatal uptake of methyl mercury from sea food and the resulting loss of intelligence causes diminished economic productivity that persists over the entire lifetime of affected children.

To better understand the pathways of mercury from anthropogenic emissions to bio-accumulation in marine biota we developed an Eulerian three dimensional multi-media chemistry transport model (MECOSMO) that includes atmosphere, ocean, and ecosystem. The model includes a complete representation of the marine ecosystem from phytoplankton up to higher trophic levels, including fish. We use MECOSMO to simulate the spatial and temporal variability of mercury accumulation in fish in the North- and Baltic Sea. Based on a 60 year hind cast, we determine the natural variability of the system. Moreover, the model is used to project the impact of future perturbations in the system (i.e.: emission reductions, climate change, nutrient control) on the mercury accumulation in sea food. Thereby, supporting the implementation of the Minamata Convention on Mercury on a regional scale.

This work is still ongoing and the results of our model study will be presented for the first time at the ICMGP2017.

TP-038

METHYLATION AND BIOACCUMULATION OF MERCURY FROM ‘NEW’ AND ‘OLD’ SOURCES IN ESTUARINE SYSTEMS

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Mercury (Hg) pollution remains a concern for human and wildlife populations worldwide. Anthropogenic input of Hg to coastal ecosystems via direct atmospheric deposition and land runoff is expected to decline if negotiated mitigation efforts are implemented. To what extent and within what timeframe the levels of Hg in estuarine fish will be reduced to levels where it no longer poses a threat to human and wildlife health however remains uncertain. One major factor contributing to this uncertainty is the poor understanding of how Hg in recent inputs (‘new’ Hg) differs in availability for methylation and bioaccumulation in comparison to legacy Hg (‘old’ Hg) stored in the sediments. We have conducted mesocosm studies in which the bioavailability of different geochemical pools of Hg was studied under different nutrient and terrestrial matter loading regimes. The systems consisted of intact sediment cores (diameter of 0.63 m) that were placed in 5 m high mesocosm columns filled with brackish water. We then quantified the methylation, demethylation and bioaccumulation of two sets of inorganic Hg (HgII) and methylmercury (MeHg) isotope tracers. One set was added to the sediment (as MeHg and HgII bound to organic matter and HgII added as black cinnabar, β-HgS(s)) representing ‘old’ inputs of Hg, and one set was added as aqueous HgII and MeHg to the water column representing ‘new’ inputs of Hg. In this presentation, we will summarize the key findings from these studies (Jonsson et al., 2014, Nature Communications, Nguyen et al., 2016, Environmental Science and Technology, Jonsson et al. 2017, Science Advances) and discuss how this knowledge can be implemented in predicting future trends in Hg pollution and in the management of contaminated sites. We show for example that the chemical speciation of HgII solid/adsorbed phases controls the sediment Hg pool’s contribution to MeHg, but that input of MeHg from terrestrial and atmospheric sources bioaccumulates to a substantially greater extent than MeHg formed in situ in sediment. Based on the results we also predicted 3-6 times enhanced concentration of MeHg in zooplankton in coastal areas following scenarios with 15–30% increased terrestrial runoff (as suggested for parts of the world due to climate change).

TP-039

ESTIMATION OF AIR-WATER EXCHANGE FLUX OF MERCURY FROM OCEAN IN NORTHEAST ASIAN REGION

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Mercury differs from other heavy metals in that it continuously goes through the deposition and re-emission cycle in the environment. Mercury mainly exist as reactive Hg (Hg2+) in either dissolved or particulate phase in aquatic system. Reactive mercury can be converted to methyl mercury (MeHg) which readily bio-accumulates in aquatic food chains resulting in adverse health effects in human and wildlife, or re-emitted after reduction to elemental mercury. Emission from ocean surface is a great contribution to natural Hg emissions inventory and is an important pathway for removing Hg mass from aquatic system; therefore, quantifying the exchange flux between air and ocean surface is critical for understanding Hg fate and transport in environment. This study was initiated to estimate air-water exchange flux from ocean in Northeast Asian region. Air-water exchange of Hg is strongly dependent on DGM (Dissolved Gaseous Mercury) concentration in water. However, DGM has very low concentration and is supposed to have significant temporal and hourly variation because reduction and oxidation rate constants vary with UV radiation intensity. In this study, we measured total mercury (TM), reducible Hg (RM), and DGM concentrations during three cruises campaigns in open ocean in Northeast Asian region, and obtained the relationships among three Hg species. RM concentration ranged 20-55% of TM concentration, and a statistical correlation between TM and RM/TM ratio was observed. Spatial map of TM concentration in Northeast Asian Ocean was first obtained based on measurements from this study and from literature review, and RM concentration was then calculated based on empirical equation acquired between TM and RM/TM ratio. At the same time, laboratory experiments were carried out to identify the rate coefficients of Hg reduction and oxidation under various UV radiation intensity. DGM concentration will be calculated using reduction and oxidation reaction constants and calculated RM concentration, and air-water exchange flux will be estimated using two-film theory. Detailed results will be showed at the conference.

TP-040

PHOTODEMETHYLATION OF METHYLMERCURY IN SEAWATER MEDIATED BY DISSOLVED ORGANIC MATTER

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Dissolved organic matter (DOM) exerts a strong influence on the rate of methylmercury (MeHg) photodemethylation in ocean water. This MeHg photodemethylation can occur via two potential pathways in seawater: photodemethylation of MeHg by photochemically produced reactive intermediates (PPRIs; 1O2, ^{3}DOM*, e^{-}aq, ·OH) and direct photodemethylation of MeHg-DOM complexes via intramolecular charge transfer. We investigated the potential mechanisms of DOM mediation of MeHg photodemethylation by measuring the demethylation rate constants in artificial seawater under UV-A (365 nm), in the absence and presence of Suwannee River Humic Acid (SRHA) and Pony Lake Fulvic Acid (PLFA). The concentration of MeHg decreased with increasing UV exposure time, and the photodemethylation process followed pseudo-first order kinetics. A predominance of MeHg-SRHA and MeHg-PLFA species over MeHgCl increased the photodemethylation rate constant by 2-5 times that of MeHgCl. The presence of SRHA decreased the concentration of MeHg by 54% in absence of a quencher (0.010 h^{-1}), whereas it decreased by 38% and 20% in the presence of the ·OH quencher (0.0057 h-1) and 1O2 quencher (0.026 h^{-1}), respectively. Amendment with PLFA decreased MeHg by 70% in absence of a quencher (0.016 h^{-1}), and by 64% and 50% in presence of the ·OH quencher (0.0125 h-1) and 1O2 quencher (0.0085 h^{-1}), respectively. These results imply that microbial fulvic acid (FA) has higher photosensitization effects than terrestrial humic acid (HA), and 1O2 mediation is more dominant than ·OH mediation. Additional experiments with other model compounds, aimed at identifying the role of functional groups in HA and FA, showed that 1) photodemethylation was faster in the presence of aromatic thiols (thiosalicylic acid, 0.37 h-1) than aromatic carboxyls (salicylic acid, 0.010 h-1) or nonaromatic thiols (glutathione, 0.019 h-1), and 2) the photodemethylation rates of aromatic carboxylates and nonaromatic thiols were similar to those of SRHA and PLFA. The rate constants were lower in the presence of the ·OH quencher (0.0066 h-1 for glutathione and 0.0055 h-1 for salicylic acid) than with the 1O2 quencher (0.012 h-1 for glutathione and 0.0074 h-1 for salicylic acid). The rate constants for thiosalicylic acid (aromatic thiols) were similar for both quenchers (0.45 h-1 for 1O2 quencher and 0.40 h-1 for ·OH quencher) and these values were comparable to those determined without quenchers, implying that the role of PPRIs is not significant. The overall rate constants were compared to those for natural seawater to obtain insights into the photodemethylation mechanisms occurring in marine water.

TP-041

BIOMONITORING ALONG THE FRENCH COASTLINE: COULD MERCURY ISOTOPIC COMPOSITION INDICATE A TEMPORAL CHANGE IN HG REACHING THE COASTAL ZONE?

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Mercury (Hg) is a natural element toxic to all living organisms. Its ocean biogeochemical cycle is dominated by atmospheric deposition, which human activities contribute to disrupt significantly, and to a lesser extent by riverine discharge. This element is bioamplified and bioaccumulated in marine food webs. Since mercury concentrations in some coastal animal species of high trophic level approach sanitary thresholds, understanding biogeochemical processes and mechanisms leading to these elevated Hg concentrations becomes important. The stable isotopic geochemistry of metal is indeed a very promising way to trace processes and transfers from one mercury biogeochemical reservoir to another (Sonke and Blum, 2013). The stable isotopes of Hg undergo fractionation that can be either dependent (MDF) or independent (MIF) of their mass, thereby potentially enabling to track biological (MDF) and transfer processes between geochemical reservoirs (MIF). Their coupling with stable isotopes of carbon (C) and nitrogen (N) in biota, clarifies the functioning of trophic networks, and the bioaccumulation processes of contaminants such as Hg.

Since the 1970's, the ROCCH, a Mussel Watch-like program, tracks contaminants on the French metropolitan coastline using of bivalves as quantitative indicators of coastal chemical contamination. The aim of the project was to map for the first time and on a national scale the temporal and spatial isotopic variations of Hg, C and N. This work also attempts to better discriminate the sources and trace the origin of Hg in bivalves (e.g., is Hg from the global ocean, associated with fluvial OM, or atmospheric local deposition...).

Along with its companion paper dealing with Hg speciation, we will present here mercury isotopic composition data for our entire dataset. The initial results of mercury speciation suggest that total Hg is not a limiting factor for Hg methylation (Briant et al., 2016). Thus, with global change and the predicted temperature rise, the associated increase in bacterial activity and eutrophication of coastal waters could increase MeHg production as proposed by Soerensen et al. (2016). Specifically, preliminary Hg isotope data show a regional signature (Atlantic Ocean vs. Mediterranean Sea), which may come from different trophic regimes as shown by N and C stable isotopes. In contrast to marine-influenced sites without temporal variations, river-influenced sites show temporal δ202Hg increase (e.g., -0.5 to +0.25‰), suggesting a decadal change in the origin of Hg reaching the ocean.

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TP-042

COASTAL EROSION AS A SOURCE OF BIOAVAILABLE MERCURY TO THE MARINE ENVIRONMENT

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Mercury can be introduced into the marine environment in many different ways. In the case of the Baltic Sea, rivers and atmospheric deposition are predominant ones. However, in the face of ongoing climate change new potential source, coastal erosion, starts to become more significant and currently is considered as third most important source of mercury in the Gulf of Gdansk region. It is especially crucial given coastlines where due to increased occurrence of extreme natural phenomena such as storms, heavy rains, floods, the erosion processes along the coast begin to increase. Particularly vulnerable are cliff coasts which cover about 30% of the length of Polish coastline.

In recent studies considering coastal erosion as a source of mercury to the Gulf of Gdansk, annual loads of Hg were estimated. The aim of this study was to evaluate the amount of labile mercury in cliff sediments. Samples were collected in years 2015-2017 from four cliffs situated in the region of the Gulf of Gdansk, southern Baltic Sea. From each cliff 3 cores (0-65cm) were collected: from the slope of the cliff, and its top. Additionally sediments from the beach and coastline waters (1 m depth) were collected. Samples were kept in -20C until analysis. Later sediments were lyophilized and homogenized before mercury analysis. Mercury speciation was performed on DMA-80 mercury analyzer using thermodesorption method. It enabled to distinguish between labile and stable forms of Hg in sediment cores.

Cliffs along southern Baltic coast comprise mostly of Pleistocene glacial tills (boulder clay) thus mercury concentration in this kind of sediments was the most important one to focus on. Studies indicate that in boulder clay about 60% of mercury is present in bioavailable, labile form. Median concentrations of mercury in collected sediments samples did not exceed natural background values. Although taking into consideration the total mass of sediment which is annually introduced into the Baltic sea, and large masses introduced each time during natural extreme phenomena, it can be regarded as a significant route through which Hg enters the marine environment. High content of labile form suggests that mercury form coastal erosion processes can influence the marine trophic chain.

TP-043

MERCURY SPECIATION AND RETENTION IN A SALT MARSH UNDERGOING LONG-TERM FERTILIZATION

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Experimental plots in Great Sippewissett Marsh (Falmouth, MA USA) have been undergoing long-term (>42 years) fertilization through the application of commercially available, sewage sludge-based fertilizer. This material, while delivering organic carbon and nitrogen to the marsh, supplies elevated amounts of mercury (Hg) and other metals as well. This experiment provides a unique opportunity to test hypotheses regarding the Hg-related response of coastal marine ecosystems to eutrophication as well as assess the efficacy of salt marshes to act as sinks for increased loadings of Hg to the coastal zone. We found Hg inventories in the salt marsh sediments that were usually equivalent to, or greater than, the inadvertent loadings from fertilizer in the treatment plots and from the atmosphere in the control plots, and in both high and low sections of the marsh. We also found that the control plots appeared to retain all atmospheric Hg loadings, though their faithfulness as historical archives maybe questionable. Likewise, the distribution of Hg in the fertilized plots appeared to be shifted relative to our reconstructed history of loadings, implying either some level of Hg mobility or inaccuracies in our reconstructions. The abundance of monomethylmercury (CH3Hg+) within the plots varied dramatically with the amount of fertilizer applied as well as sediment total sulfur, with higher percentages of Hg as CH3Hg+ and amounts of S in the control plots, and lowest percent CH3Hg+ and S in the most fertilized plots. Artifact CH3Hg+ formation was observed through the use of Hg stable isotope tracing during extraction and analysis and found to dominate uncorrected measured CH3Hg+ in the plots undergoing the highest level of fertilization.

These results showed no systematic change of Hg mobility relative to control plots other than the increased load of Hg. Thus, it would appear that New England salt marshes possess a strong ability to retain Hg loadings and that this ability is resistant to degradation by low- to moderate-level eutrophication. Finally, the prediction made by Driscoll and colleagues that eutrophication leads indirectly to less CH3Hg+ production appears borne out in this particular ecosystem.

TP-044

SPATIAL AND TEMPORAL CHANGES IN TOTAL MERCURY AND METHYLMERCURY CYCLING IN LONG ISLAND SOUND

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Mercury cycling in shallow coastal bays and sounds remains poorly understood even though these are important in terms of local and subsistence fisheries. Long Island Sound (LIS), a temperate shallow estuary with an average depth of ~30 m, receives riverine discharge exclusively on its north shore and from the East River flowing through New York City at its western end. Approximately 90% of riverine influx to LIS is derived from the 653.59km-long Connecticut River, originating in Canada and entering LIS towards its eastern boundary. Water of LIS exchanges with the Atlantic Ocean primarily via a narrow, deeper (~50 m) passage, the race, situated on LIS eastern end, where there are strong tidal currents. A previously constructed budget for LIS assumed values for tidal exchange and in situ production, which have not been supported by rigorous measurements. Our recent study measured total mercury (THg) and methylmercury (MeHg) during 3 cruises that took place in May, August and November of 2016 along the transect connecting the north shore of LIS at the mouth of Connecticut River and the south shore of LIS at Orient Point (Long Island, NY). Water collected with Teflon-lined Niskin bottles from 3 depths (e.g. surface, mid and bottom) at 5 stations along the transect at low and high tide, was transferred using trace metal clean approaches into 2L Teflon bottles. During the cruise in November, water was also sampled during incoming and outgoing tides. Collected water was filtered via combusted quartz fiber filters. Both the filtrate as well as the collected particulate matter were analyzed for THg and MeHg. While analyses are ongoing, our initial results show that in spring and in the fall, the dissolved as well as the particulate MeHg concentrations were elevated near the river mouth as well as 2-5 m off the bottom. Spatial and temporal Hg distribution patterns for the filtrate and particles are here used to update the previous budget, while better constraining the importance of seasons, tides, and exchange across the race. Mass balance modeling was applied to simulate the effect of tide on the THg and MeHg cycling in the LIS.

TP-045

MERCURY SPECIES FLUXES FROM SEDIMENT: INSIGHTS FROM COMPARISON BETWEEN 224RA/228TH DISEQUILIBRIUM AND CORE INCUBATION

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Sediment is the main site of mercury methylation. Accurate quantification for methylmercury (MeHg) flux at the sediment-water interface is vital to better understand the biogeochemical cycling of mercury, especially the toxic MeHg species. Methylmercury is non-conservative in aquatic systems and many factors affect its concentration. Traditional approaches, such as core incubation, are hard to maintain at the in-situ conditions, leading to over/underestimation of benthic fluxes. The 224Ra/228Th disequilibrium method for tracing the transfer of dissolved substances just across the sediment-water interface, has proven to be a reliable proxy to quantify the benthic flux. In this study, both 224Ra/228Th disequilibrium and core incubation methods were applied to examine the benthic fluxes of both 224Ra and MeHg in Barn Island, Connecticut, USA (a wetland) from May to August, 2016. The results showed that the two methods were comparable for 224Ra but contradictory for MeHg. The radiotracer method indicated sediment was always a dominant source of both THg and MeHg. Core incubation produced similar results in May and August but an opposite pattern that sediment was a sink of MeHg in June and July, which was contrary to the evidence of significant MeHg gradients at the sediment-water interface. Overall, we conclude that the 224Ra/228Th disequilibrium approach is preferred for estimating the benthic flux of MeHg and that sediment is indeed an important MeHg source in this wetland.

TP-046

BIOACCUMULATION OF MERCURY ON FISHES IN MINAMATA BAY, BASED ON FOOD WEB ANALYSIS AND CARBON AND NITROGEN ISOTOPE ANALYSIS

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From 2010 we have been researching the bioaccumulation of mercury in several fishes in Minamata Bay and surrounding areas in Yatsushiro-Kai, Kumamoto, Japan. We selected several sampling points that showed different environmental conditions, species composition and food web patterns. For the determination of feeding types of 60 species fishes (600 samples) sampled by gill net, we measured mercury levels of each sample and distinguished food habit, such as carnivore, omnivore, herbivore and detritivore from direct observation and DNA checking of fish gut contents. At this time, we introduced a stable isotope analysis for checking the food history and feeding habits of dominant fish. In about 300 individuals of 30 species of dominant fish selected from the 600 samples, we measured the stable nitrogen and carbon isotope ratios (δ15N, δ13C) of each sample. We also measured δ15N and δ13C of phytoplankton, zooplankton and benthic microalgae. Checking the food items in the gut of fishes, more than 80% were carnivorous, and showed different selectivity of food items, such as fish and crustacean. From the results of stable isotope ratios, benthic fish tended to show

a higher ratio of δ13C. Usually benthic microalgae evidenced a higher ratio of δ13C than planktonic microalgae, and the ratio conservative through the food chain. In general, δ15N increases through the food chain with +3 to +4 ‰ enrichment per trophic step. In these data, carnivorous fishes of benthic and pelagic type showed medium and high ratios of δ15N. From comparing the stable isotope ratio to the mercury concentration of fishes, all of the high-mercury fishes belonged to benthic and carnivorous types. We consider the joint method of food web analysis and stable isotope analysis to be useful for understanding the mechanism of mercury bioaccumulation through the food web.

TP-047

METHYLMERCURY AT THE SEDIMENT-WATER INTERFACE: INSIGHTS FROM A UNIQUE SAMPLING REGIME

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Sediments are the largest repository for mercury (Hg) in estuarine systems, but their role as a source of methylmercury (MeHg) to the coastal water column is under critique. We used a unique sampling approach to examine particulate MeHg exchange between estuarine sediments and the water column via resuspension over naturally relevant tidal and storm shear stress conditions. The resuspended fraction was collected using a Gust Microcosm Erosion System which induces step-wise increasing shear stresses to undisturbed sediment cores. The cores were collected from an upstream (8.1 ppt) and a downstream location (28.4 ppt) in the Delaware River. Within each location two sites were selected, one organic carbon (OC) poor and one OC rich. Particles were collected from the erosion effluent and analyzed for MeHg, total Hg, chlorophyll a, and C, N, S concentration and isotopic signature. We also collected a traditional bulk sediment sample (0-4 cm homogenized) to compare these results to. The results suggest that easily eroded particles have a different Hg composition than the bulk sediment for both OC conditions. At high OC sites, the resuspended fraction had less MeHg than the bulk sediment while the opposite was true for the low OC sites. The resuspended particles were similar to the suspended particulate MeHg burden at the more terrestrial site, but differed from both the sediments and the water column at the more marine site. This could be due to a higher abundance of living plankton at the more marine site, as suggested by high concentrations of chlorophyll a in the 0.2-20 µm size fraction, that would likely not be interacting with the surface sediments. The C isotopic signature for particles at the marine site was -21‰ indicative of marine phytoplankton, whereas the terrestrial site δ13C was -24.0‰ representing a mixture of marine and terrestrial carbon. This suggests that the MeHg dynamics at the sediment-water interface are distinct from the bulk sediment, and sampling of the bulk sediment does not provide an accurate reflection of the potential input of MeHg to the water column from resuspension. Therefore, to fully understand benthic-pelagic coupling in terms of MeHg in coastal ecosystems, the near-surface particulate MeHg should be sampled and considered when relating sediment-MeHg contributions to the overlying estuarine water columns.

TP-048

IMPACT OF PELAGIC FOOD WEB STRUCTURE ON MONOMETHYLMERCURY BIOACCUMULATION IN COASTAL SEAS – A BALTIC SEA CASE STUDY

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Monomethylmercury (MeHg) is a potent neurotoxin that has a unique ability to biomagnify in aquatic food webs to harmful levels. Previous studies have shown that MeHg preferentially binds to organic compounds containing reduced sulfur groups (thiols). Thus, the concentration and composition of dissolved organic matter (DOM) play an important role in chemical speciation and bioavailability of MeHg. Terrestrial input of DOM furthermore promotes the growth of heterotrophic bacteria and therefore increases their share of the biomass production in the bottom of the pelagic food-web.

The Baltic Sea is an ideal study area for processes responsible for mercury transformation and its pathway in the environment due to large differences in the concentration of terrestrially derived DOM between the north and the south. Hence, different food web structures are present with bacteria-based (microbial) food web in the northern and phytoplankton-based (herbivorous) in the southern areas. As a result of elevated input of DOM in the northern basins and the differences in the food web structures, we hypothesize that MeHg concentrations in the higher trophic level of the pelagic food web (zooplankton) significantly differ between the two regions.

In this study we determine concentrations of MeHg in water and plankton samples obtained from different subbasins within the Baltic Sea using gas chromatography inductively coupled plasma mass spectrometry and calculate bioaccumulation factors through the food web up to zooplankton. We furthermore determine the speciation of sulfur by S-XANES (sulfur X-ray absorption near the edge structure) and identify dominant individual low molecular mass (LMM) thiols using liquid chromatography electrospray ionization mass spectrometry. These data are used to assess MeHg bioavailability and biomagnification from the dissolved phase and up to zooplankton.

Initial results from 2015 suggest that dissolved MeHg concentrations are slightly higher in the southern Baltic offshore surface waters (24±16 fM) than in the north (11±11 fM). However, we find that MeHg concentrations in plankton and the bioaccumulation factors decrease along the north-south gradient. This could be tightly connected with the microbial food web structure. With additional speciation data from 2016 cruise campaigns we will further address MeHg bioavailability and elucidate on how it affects the bioaccumulation process.

TP-049

MERCURY PARTITIONING AND SPECIATION IN NORTHERN GULF OF MEXICO ESTUARIES

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Improving our understanding of mercury cycling within estuaries is an important step in modeling mercury uptake by biota and quantifying mercury fluxes to the coastal ocean. We sampled 11 U.S. rivers (Suwannee, Apalachicola, Escambia, Mobile, Pascagoula, Pearl, Mississippi, Lower Atchafalaya, Sabine, Trinity, and Brazos rivers) discharging into the Gulf during Spring and Fall 2012. We measured total and methyl mercury (MeHg) concentrations in particulate and filtered phases as well as other parameters including total suspended solids, dissolved oxygen, and dissolved organic carbon. Mercury concentrations varied along salinity gradients with most systems characterized by mid-estuary maxima in MeHg concentrations. The mean fraction of total mercury as MeHg in each estuary ranged between 0.8 and 3.4%. We found significant correlations between particulate total mercury and total suspended solids. Seasonal differences in the partition coefficients of total mercury appear to be driven by changes in the concentration of filtered mercury.

TP-050

MERCURY CYCLING IN A CHESAPEAKE BAY SALT MARSH: THE IMPACT OF PHRAGMITES AUSTRALIS

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Wetlands are known to be active sites of mercury (Hg) methylation and can be important sources of methylmercury to downstream systems and the food web. Salt marshes play a multifaceted role in estuarine ecosystems, such as cycling nutrients, providing habitat and mitigating floodwaters. Invasions of plants such as Phragmites australis have raised concerns over how invasive plants impact wetland ecosystem function. The role of P. austalis is complex. In some cases its presence may expand habitat, but in others habitat quality is decreased resulting in an altered food web.

Apart from its role in nitrogen cycling, our understanding of the impact of changes following a P. australis infestation on biogeochemical cycles is not well known. In P. australis patches of the Rhoade River Salt Marsh in the Chesapeake Bay Md, we have observed dramatic differences in sulfur and carbon cycles between P. austalis communities and other plant types. We believe this is in large part because of the active pumping of oxygen to the root zones. Sulfide is all but eliminated in peat pore water surrouning the P. australis.

Concentrations of mercury in the peat pore water around the plant roots are much higher than found in other plant communities in the marsh. Concentrations of methylmercury in the pore water are as high or higher than found in pore water of the other plant communities in the marsh. Given the differences in redox condition, Hg cycling is unlikely to be the same, driven by differences in Hg supply and microbial activity. In this presentation we will first examine factors influencing Hg cycling in the P. australis infested Rhode River Marsh. Salt marshes are import sources of carbon estuaries. Export of dissolved organic matter is substantial, and being located on the fringes of the marsh, P. australis dominated patches perhaps have a greater impact on the type and amount of carbon exported, and hence the Hg and meHg exported, than other plant communities. We will discuss C and Hg export from the Marsh and examine any linkages back to plant community source.

2b: Sources and cycling of mercury in freshwater ecosystems

TP-051

MERCURY FATE AND CYCLING IN RIVER SEDIMENT FOLLOWING A FLY ASH RELEASE IN THE DAN RIVER, USA

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Following recent spills of coal combustion residue (fly ash) into rivers of the United States, questions have arisen as to the impact of this material on the ecosystem. Following the Dan River spill in 2014, we undertook a study to investigate how fly ash impacted mercury cycling in riverine sediments. First we used particle size separation methods and low level mercury analysis to test for the presence of fly ash. Second we assessed if the presence of fly ash affected total mercury (T-Hg) concentrations in sediment, as this system had already been impacted by industrial releases. We next tested how ash might impact Hg partitioning between sediment and water. Finally we examined whether the presence of ash impacted methylmercury concentration in sediment and sediment pore water.

We found that analyzing discrete particles size fractions for total mercury (T-Hg) is an effective means of determining the presence of fly ash in the sediment. Analysis of Hg concentrations in bulk phase sediment was not nearly as discerning. When ash was present in sediment, T-Hg concentrations (as defined by the sum of all mercury species) in sediment pore water were not significantly different than in pore water from sediment containing no fly ash. In the case of the methylated Hg species (MeHg); experimental enrichment of sediment with fly ash resulted in increased MeHg concentration with increasing ash concentration. Methylmercury concentrations also slightly increased in water overlying the sediment enriched in fly ash suggesting that the presence of ash increases the contribution of MeHg to overlying water.

TP-052

VERTICAL AND SEASONAL VARIATION OF MERCURY METHYLATION AND SPECIATION IN A EUTROPHIC KETTLE LAKE

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Mercury methylation in the water column of lakes and the ocean may be an important source of monomethylmercury (MMHg), which bioaccumulates in food webs and poses a potential health threat to wildlife and humans. To better understand MMHg synthesis in the water column, the vertical distribution of mercury (Hg) species were examined in a spring-fed, eutrophic lake in western Ohio, USA. Crystal Lake is seasonally stratified, with a sulfidic profundal zone during the summer and fall. Ambient concentrations of monomethyl-, elemental, and total Hg were profiled almost monthly throughout the water column for one year. Water from five depths of the lake (surface water, chlorophyll maximum, above and in the MMHg maximum, and sulfidic bottom water) was amended with isotopically enriched inorganic Hg and MMHg, and incubated at the respective depths to quantify rates of Hg methylation and MMHg demethylation. Ambient concentrations of total Hg and MMHg were greatest at the oxic/anoxic boundary layer. Mercury was methylated in both oxic and anoxic portions of the water column, although rates were greatest in the boundary layer. These results suggest that redox transition zones in the water column are an important source of bioavailable MMHg and that methylation also occurs in oxic water, although the mechanism is unknown.

TP-053

UPTAKE AND VOLATILIZATION OF GASEOUS ELEMENTAL MERCURY BY PADDY RICE

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Wetland is an important sink of mercury, and its reducing substrate favors for the production of gaseous elemental mercury. In order to adapt to the anoxic condition, wetland plants usually have developed aerenchyma to transport oxygen from the atmosphere to the roots for cellular respiration. In this study, a typical wetland plant paddy rice is used to study whether its root and aerenchyma can also be a channel for the transport of rhizosphere gaseous mercury into the atmosphere. If it is, what are the mechanisms underlying. In this paper, the roots of rice were separated from the shoots by a well-air-tighten chamber. Roots were exposed to saturated mercury vapor in root chamber, then the gaseous mercury volatilized from the leave chamber was absorbed by the active carbon absorbent. The results showed that gaseous elemental mercury could be absorbed by rice roots and be transported to shoots. The mercury of roots was negatively correlated with root porosity (R=0.8309, P<0.01), while the mercury in the aboveground tissues showed a positive correlation with root surface area and root volume (R = 0.896, P <0.01; R = 0.871, P <0.01; respectively). The results also indicated that the mercury absorbed by the roots could be volatilized into the atmosphere through the leaves. The volatilization of the mercury from the leaves was increased positively with the leaf area (R = 0.897, P <0.01). There was a significantly positive correlation between the mercury volatilization per unit leaf area and transpiration intensity (R = 0.73, p <0.01). The results have proved that rice roots can not only absorb gaseous elemental mercury, but also transfer mercury to the aboveground, and then released into the air through the leaves of the stomata. The results provided a scientific basis for further investigations of revealing mercury behavior and regulation mechanisms in wetland ecosystems.

TP-054

SINK OR SOURCE? MERCURY LOADS INTO AND OUT OF THE SEASONALLY STRATIFIED HELLS CANYON RESERVOIR COMPLEX, IDAHO AND OREGON, USA

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Anoxia in the hypolimnion of lakes and reservoirs can promote the conversion of mercury (Hg) to the more toxic methylmercury (MeHg) form. In the 200-km Hells Canyon Reach of the Snake River along the Idaho-Oregon border, three deep (up to 90 m) reservoirs seasonally stratify for months at a time, creating anoxic conditions that promote MeHg production in the hypolimnion. As a result, both Idaho and Oregon have listed this reach of the Snake River as impaired for Hg, with fish-tissue samples regularly exceeding Idaho's human health fish tissue criterion of 0.3 mg/kg wet weight.

In 2014, the U. S. Geological Survey and Idaho Power Company initiated a collaborative investigation of Hg cycling and fate in the Hells Canyon reach. Primary research questions for this project include understanding the mechanisms promoting MeHg production in the hypolimnion, and the fate of the MeHg accumulated in the hypolimnion subsequent to

reservoir destratification and mixing. To help answer these questions, the mass loadings of Hg and MeHg into, within, and out of the Hells Canyon complex of reservoirs were estimated using discrete water-quality data and streamflow into and out of each reservoir.

Water samples were collected biweekly from four reservoir inflow/outflow locations between 2014 and 2016 and were analyzed for dissolved and particulate Hg and MeHg. Streamflow data collected continuously at the inflow and outflow of each of the three reservoirs were used to compute mean daily streamflow values during the sampling period. Using the R software package rloadest, regression models were developed to relate instantaneous Hg and MeHg loads to daily streamflow and seasonal variables. Loads were computed at various time steps over the sampling period to estimate the mass balance for each reservoir in the Hells Canyon Complex and for the complex as a whole. Results indicate that Hg inflow is ~2.7x greater than outflow, and MeHg inflow is ~2x greater than outflow, despite clear production and accumulation of dissolved MeHg in the hypolimnion within the reservoir complex. Thus, overall, the reservoirs act as Hg and MeHg sinks. Findings from this study are intended to help manage the Hells Canyon Complex to minimize downstream export of Hg and MeHg.

TP-055

VERNAL POOLS AS METHYLMERCURY SOURCES TO FOREST FOOD WEBS: EXPORT VIA EMERGENT INSECTS

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Vernal pools are ephemeral wetlands that provide essential habitats for amphibians. Our previous work demonstrated that inorganic mercury (HgI) in leaf litter was converted to methylmercury (MeHg) after spring flooding in a New England vernal pool. We further showed that this MeHg was bioaccumulated by resident invertebrates, including insect larvae. Based on these findings, we hypothesized that insect emergence might provide a vector for transferring MeHg into to the surrounding forest; therefore, we investigated the export of MeHg from a vernal pool via emergent insects. In the first year of the study we surveyed the types of emergent insects inhabiting the pool and measured their MeHg concentrations. In the second year we quantitatively collected insects in order to determine the seasonal flux of insect-associated MeHg. Duplicate emergence traps were deployed between May 5 and Aug 5, 2015, which spanned the period between full flooding in the spring and drying out in the summer. Insects were collected on a weekly basis. After insect samples were dried and massed, they were analyzed for MeHg and total mercury (HgT) concentrations using acid extraction and CVAFS. Our results showed similar MeHg concentrations for insects collected in the two traps, 34±6 and 29±9 mg/g, but different patterns of emergence led to differences in MeHg export rates over the study period. The average insect-associated MeHg export rates in the two traps were 40 and 140 pg MeHg/m^2 d. The total amounts of MeHg exported were 3 and 14 ng MeHg/m^2.   This export represents about 0.1% of the HgI that was deposited onto the pool via leaf litter in the fall. Considering the abundance of vernal pools in some forested landscapes, our results suggest that these wetlands may be important sources of MeHg to forest food webs.

TP-056

MERCURY DISTRIBUTION AND VARIATION IN LAKE ERIE

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North American Laurentian Great Lakes are the largest surface freshwater system in the world presenting a valuable recreational and commercial fishery among many other benefits. Mercury levels in fish from Lake Erie, the shallowest of the five lakes, are weakly increasing over the last two decades. We conducted extensive analysis total mercury (THg) and methylmercury (MeHg) of water, sediment, seston and 3 fish species collected from 10 sites in the three basins of the lake (western, central and eastern) over a four month summer period to understand mercury dynamics in the system. Overall, our observations and reports in the literature suggest that THg have declined in the sediments of all three basins during the last two decades. THg and often MeHg water and sediment concentrations remain higher in the western basin than the central and eastern basins. This is especially true for the sediment, which may be acting as a continual source of Hg to both the water column and subsequently the primary biota of the basin. Despite the western basin having significantly higher Hg in the abiotic compartments, the %MeHg was often lower in the west and increased eastward, indicating that complex factors are contributing to higher MeHg production and comparable bioaccumulation in biota in the central and eastern basins. These data can be used for future reference as well as for input into Hg dynamics models, which require a certain minimum of accurate empirical data to be of use to aquatic ecology modellers.

TP-057

FRESH HUMIC AND ALGAL DERIVED ORGANIC MATTER ENHANCES METHYLMERCURY PRODUCTION IN BEAVER PONDS

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Previous studies have revealed that beaver impoundments increase methylmercury (MeHg) concentrations and alter dissolved organic matter (DOM) composition in rivers, especially in the first years after flooding. Although DOM controls mercury (Hg) availability for methylating bacteria, the impact of DOM quantity and composition in Hg methylation processes in aquatic systems remains still unclear. Here, we studied Hg methylation rates and DOM composition in 9 beaver ponds differentially aged across Sweden. We found a decrease in MeHg production with increasing age of the ponds, ponds older than 18 years featuring on average 65% lower methylation compared to those younger than 7 years. Our results show that increased MeHg concentrations in surface waters is a consequence of enhanced Hg methylation in the pond sediments. Elevated chlorophyll a concentrations found in young ponds imply internally produced organic matter as an important driver of Hg methylation. Qualitative analysis of the DOM with excitation-emission-matrix fluorescence spectroscopy, further suggests that unprocessed humic DOM also enhances Hg methylation in young pounds. Our study provide novel insights into the drivers of Hg methylation processes in boreal aquatic ecosystems.

TP-058

THE INFLUENCE OF INUNDATION AND LAKE MORPHOMETRY ON THE DYNAMICS OF MERCURY IN THE WATER AND PLANKTON IN AN AMAZON FLOODPLAIN LAKE

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Seasonal flooding changes chemical and morphometric characteristics of the tropical floodplain lakes, affecting stratification which can influence mercury dynamics. We investigate the influence of flooding on the mercury dynamics in an Amazon floodplain lake. Three points on the lake, the Solimes River and the connecting channel to the river were sampled along the annual flood-pulse. During high-water, the lake was deep (12.7 m, on average) and the area farthest from the river was stratified with low oxygen and high methylmercury concentrations ([MeHg]) at depths below 7 m (0.37 ngL-1, on average). The two sites closest to the river were destratified and the [MeHg] were lower (0.077 ng L-1, on average along all depths). At low-water, the lake was shallower (3 m, on average) and destratified, with higher oxygen concentrations, and no difference in [MeHg] along the water column at all lake sites. Independent of season, the [MeHg] in the connecting channel were higher than those in the river. The [MeHg] in phytoplankton varied in response to changes in biomass, showing a biodilution effect. Variations in lake morphometry controlled the stratification and [MeHg] in the lake during the high-water. Floodplain lakes export hypolimnetic MeHg to their associated rivers during high-water.Seasonal flooding changes chemical and morphometric characteristics of the tropical floodplain lakes, affecting stratification which can influence mercury dynamics. We investigate the influence of flooding on the mercury dynamics in an Amazon floodplain lake. Three points on the lake, the Solimes River and the connecting channel to the river were sampled along the annual flood-pulse. During high-water, the lake was deep (12.7 m, on average) and the area farthest from the river was stratified with low oxygen and high methylmercury concentrations ([MeHg]) at depths below 7 m (0.37 ngL-1, on average). The two sites closest to the river were destratified and the [MeHg] were lower (0.077 ng L-1, on average along all depths). At low-water, the lake was shallower (3 m, on average) and destratified, with higher oxygen concentrations, and no difference in [MeHg] along the water column at all lake sites. Independent of season, the [MeHg] in the connecting channel were higher than those in the river. The [MeHg] in phytoplankton varied in response to changes in biomass, showing a biodilution effect. Variations in lake morphometry controlled the stratification and [MeHg] in the lake during the high-water. Floodplain lakes export hypolimnetic MeHg to their associated rivers during high-water.

TP-059

INFLUENCES OF COMPOSITION AND CONCENTRATION OF DISSOLVED ORGANIC MATTER ON THE DISSOLVED GASEOUS MERCURY PRODUCTION IN LAKE SURFACE WATER

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The reduction of mercury in lake surface water plays an important role in the mercury biogeochemical cycle by decreasing Hg(II) availability to aquatic organisms and increasing the release of Hg(0) to the atmosphere. The formation of dissolved gaseous mercury (DGM) is a photochemical process mediated by dissolved organic matter (DOM). The aims of this study are: 1) to measure DGM concentrations and reduction (kre) and oxidation (kox) rate constants in oligotrophic, mesotrophic, and eutrophic lakes, and 2) to correlate DGM and redox rate constants with environmental variables to understand the mechanisms of DGM production in surface lake water. The composition of fluorescent DOM in surface water samples was also analyzed using excitation-emission matrix (EEM) fluorescence combined with a parallel factor (PARAFAC) model. Three target monitoring sites were chosen based on self-organizing map (SOM) results: Jangsung Lake (JSL) is an oligotrophic lake surrounded by forest (85% of catchment area), Kumho Lake (KHL) is a mesotrophic lake located by the coastal sea, and Yeongsan Lake (YSL) is an eutrophic lake located downstream of Gwangju city. The EEM-PARAFAC identified three components of DOM in surface lake waters: humic-like (C1), fulvic-like (C2), and protein-like (C3). Seasonal monitoring results showed that surface water DGM was highest in the oligotrophic JSL and lowest in the eutrophic YSL. The site trend of DGM agreed well with the site trend of the net reduction rate: kre/kox was highest in the JSL and lowest in the YSL. The Pearsons correlation analysis results demonstrated a significantly positive correlation between kre/kox and %C3 and a significantly negative correlation between kre/kox and %C1, indicating that the net reduction of Hg(II) is promoted by protein-like DOM or inhibited by humic-like DOM. Currently, we are carrying out field measurements of individual kre and kox to determine which reaction (i.e., reduction or oxidation) rate varies as a function of DOM composition.

TP-060

MERCURY GEOCHEMISTRY IN A UNIQUE TROPICAL AGRICULTURAL WETLAND ECOSYSTEM, INDIA

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Mercury pollution of the aquatic ecosystems, especially agricultural wetlands is of major concern owing to the highly toxic and persistent nature of mercury and subsequent accumulation in the aquatic biota. The present study was conducted in a unique tropical agricultural ecosystem, situated in the South west coast of India, where rice cultivation is practiced below sea level. Most of these areas are water logged throughout the year and subjected to flood during monsoon period. The geochemical analysis revealed the acidic as well as anaerobic nature of the system. The THg content in the soil and various tissues of rice plants were studied during the entire rice growing season (i.e., from 30th day to 120th day).The analysis was done using Direct Mercury Analyzer (DMA 80, Milestone, USA). The mercury concentration in the soils were within the range of uncontaminated sites prescribed by USEPA. The mean THg concentration obtained for soils is 0.088mg/kg. The average concentration of THg in the plant tissues followed the pattern root>leaf>grain>husk>stem. The correlation analysis as well as translocation factor supported the possible translocation of mercury from the root to the other parts of the rice plant. The comparative study showed that, the THg concentration obtained in the present study (0.0219 mg/kg) is less than the values reported in the literature. However it slightly exceeds the maximum limit (0.02 mg/kg) recommended by the Chinese National Standard Agency for food stuff. Since studies on mercury cycling in the aquatic ecosystems of tropical countries is very less, it is highly crucial to develop a thorough understanding of the behavior of mercury in this complex system. Varying geochemistry and enormous land area of the agricultural wetland ecosystem greatly influences the speciation of mercury and thus its toxic impacts. Hence the present study focused on the detection, bioavailability and accumulation of mercury.

TP-061

DISTRIBUTION OF THG AND MEHG IN THE WATERS OF THE MADEIRA RIVER, BRAZILIAN AMAZON

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In aquatic ecosystems the mercury (Hg) participates of numerous chemical reactions, being able to go out of the chemical form inorganic to organic form and quickly incorporate in the biota. The Madeira River has been exploited by gold mining for decades, being an anthropic route of introduction of mercury in the aquatic environment. The objective of the study is to evaluate the concentration of total mercury (THg) and methylmercury (MeHg) in the water sample (total and filtered fraction) of the Madeira River, upstream and downstream of a hydroelectric plant. Quarterly data were collected in six points (3 upstream and 3 downstream), between the years of 2013 and 2016 on the Madeira River. The water samples were collected in amber glass bottles, stored on ice and transported to the laboratory. THg and MeHg were quantified by gas chromatography coupled to cold vapor atomic fluorescence spectrometry following the methodology EPA 1631 and EPA 1630, respectively. Upstream of the hydroelectric plant, the waters of the total fraction presented the following medians for THg and MeHg, respectively: 7.21 and 0.09 ng/L (2013); 6.94 and 0.05 ng/L (2014); 5.16 and 0.11 ng/L (2015); 6.13 and 0.15 ng/L (2016). In the dissolved fraction the medians were 1.84 and 0.03 ng/L (2013); 0.70 and 0.03 ng/L (2014); 0.73 and 0.04 ng/L (2015); 0.04 and 0.04 ng/L (2016). At the downstream of the hydroelectric plant, in the total fraction, the following median values were found for THg and MeHg, respectively: 7.51 and 0.10 ng/L (2013); 5.86 and 0.07 ng/L (2014); 5.55 and 0.09 ng/L (2015); 7.17 and 0.014 ng/L (2016). In the dissolved fraction the medians were 1.76 and 0.04 ng/L (2013); 0.54 and 0.03 ng/L (2014); 0.62 and 0.04 ng/L (2015); 0.19 and 0.04 ng/L (2016). The highest THg (2103) and MeHg (2015) concentration in the water (total fraction) was observed upstream of the hydroelectric plant. The highest percentage ratio of MeHg: HgT occurred in the total fraction (9.16%) in downstream of hydroelectric (2014). There was a significant increase in the concentration of MeHg in the water (total fraction) upstream of the hydroelectric plant over the years, as well as the increase in the relation between the concentration of THg and MeHg. The highest concentration in the total water fraction was attributed to a large load of suspended particulate matter (SPM) transported by the Madeira River (annual average of SPM= 376.67 mg/L).

TP-062

HG AND MMHG CYCLING IN THE THAW LAKE SYSTEM OF QINGHAI-TIBET PLATEAU

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Thaw lakes (TLs) form a unique and widely distributed landscape in permafrost regions. The Hg biogeochemistry in climate-sensitive TLs has not been extensively investigated, but there is evidence that climate warming is altering the structure and function of TLs. In this study, we combined field measurements, in situ incubation experiments, remote sensing, and a previous water isotopic tracer study to document the characteristics of Hg and MMHg cycling in three TLs and to obtain insight into the Hg biogeochemistry of TLs under rapid climatic warming. We found that Hg(0) in water displayed higher concentrations during daytime and warm seasons and lower concentrations during nighttime and cold seasons (including under ice). But MMHg concentrations in water during cold seasons and under ice were much higher than those in warm seasons and in open water. These results suggest an important role of solar radiation on the Hg and MMHg cycle. In situ incubation experiments further confirmed that solar radiation greatly regulates Hg redox reactions and MMHg degradation. Field measurements showed that TLs were a Hg(0) emission source, and ebullition (bubbling) further increased the Hg(0) emission flux during ice-free periods. The simple Hg mass balance, incubation experiments, and previous water isotopic tracer study suggest that the groundwater and lake margin are important Hg sources to the lake water, and that the lake expansion will induce an increase in Hg(0) emission from the TL system. This study suggests that climate change may potentially affect the cycling of Hg in TL ecosystems.

TP-063

EROSION, NOT CONTAMINATION, DRIVE HIGH MERCURY CONCENTRATIONS IN THE RED DEER RIVER (ALBERTA, CANADA)

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A recent review of mercury concentration data from the Red Deer River (Alberta, Canada) revealed a number of exceedences to Canadian water quality guidelines over the past decade. Total Hg (THg) concentrations reaching as high as 860 ng/L have been measured in Michichi Creek (a tributary to the Red Deer River) and >250 ng/L within the Red Deer River itself. Concentrations >100 ng/L have been routinely observed within the Red Deer River during the open water season. These THg concentrations are generally at the upper range of values reported elsewhere, including streams and rivers impacted by legacy mining or intensive urban and industrial activities. Here we will present the results of an investigation into the potential cause(s) of these high THg concentrations.

The Red Deer River watershed covers 49,650 km2, which includes the Alberta badlands. Median (open-water) THg and total suspended solids (TSS) concentrations at sites draining the badlands were frequently more than double those of stations upstream. THg was significantly related to TSS ($r2=0.66$; $p<0.05$), indicating that THg concentrations in the Red Deer River and its tributaries are driven primarily by sediment transport. However, the concentration of THg associated with suspended sediment (Csed) did not increase downstream of the badlands, suggesting that the high THg concentrations observed are driven primarily by increases in sediment mass. In addition, THg to Al ratios of suspended sediment in the Red Deer River watershed indicate negligible (< 2) to moderate (2-5) anthropogenic enrichment.

Contributions to THg loading from upstream of the badlands were low (2-8%) despite contributing most of the flow to the river (≈70%). In contrast, four tributaries draining the badlands contributed 22% of the THg loading, despite providing only ≈9% of the flow to river. Sediment loading was highly episodic, reflecting the rapids erosional response of the Alberta badlands to precipitation events. Our results suggest that erosional processes in the Alberta badlands have played a key role in driving Hg dynamics within this river system; however, the extent to which heavy metal fluxes to the RDR have impacted biota still remains an important question.

TP-064

ABIOTIC REDUCTION OF MERCURY(II) IN SULFIDIC SUSPENSIONS: EFFECTS OF DISSOLVED ORGANIC MATTER

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Monomethylmercury (CH3Hg) is a neurotoxic pollutant that bioaccumulates and biomagnifies in aquatic food webs. In sediments, the production of CH3Hg depends on the bacterial activity of Hg methylating bacteria and the amount of bioavailable inorganic divalent Hg (Hg(II)) present. Biotic and abiotic reduction of Hg(II) to elemental mercury (Hg(0)) may limit the pool of Hg(II) available for methylation in sediments, and thus the amount of CH3Hg produced. Numerous research studies have shown abiotic reduction of Hg(II) by dissolved organic matter (DOM) and iron-containing minerals such as hydrous ferric oxide (HFO), iron carbonate, and iron sulfide. However, the authors were not unanimous about the role of surfaces in the reduction of Hg(II). A recent study has shown reduction of Hg(II) in the presence of the iron sulfide mineral Mackinawite (FeS), with significant amounts of Hg(0) formed within the first hour of reaction (Bone et al., Environ. Sci. Technol. 48, 1068110689, 2014). The data of this study is however limited and the relationship between the concentration of Fe(II) in solution and the amount of Hg(0) produced was not determined, nor was the role of DOM investigated. Here, we investigated the reduction of Hg(II) by sulfidic minerals (FeS and CdS) in the presence of dissolved iron and DOM. We showed that reduction of Hg(II) by Mackinawite (FeS) was lower (<15 % of the Hg (II) was reduced after 24 h) than when Hg(II) was reacted with DOM. We did not observe any formation of Hg(0) when Hg(II) was reacted with CdS(s) for up to four days (experiments done under both acidic and basic conditions). We also studied the reduction of Hg(II) in the presence of both FeS(s) and dissolved Fe(II) and DOM, and concluded that the solid surface of the FeS(s) had little impact on the reduction. These results will be discussed in terms of process influencing the production of Hg(0) in the presence of environmental surfaces and the reduction capability of DOM towards Hg(II) in anoxic systems.

TP-065

DISSOLVED ORGANIC CARBON (DOC) MODULATES THE SOLUBILITY AND BIOAVAILABILITY OF MERCURY AND METHYLMERCURY IN THE EVERGLADES (USA)

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Mercury (Hg) deposition and subsequent methylmercury (MeHg) concentrations within the biota of the Everglades (USA) are some of the highest in North America, leading to fish consumption advisories and wildlife toxicological concerns. However, there are spatial and temporal variations with respect to total Hg (THg) and MeHg in water, soil, and biota. Heretofore, the research conducted towards explaining this variability has emphasized the well known pathway of Hg methylation during sulfate reduction by sulfate-reducing bacteria. Although dissolved organic carbon (DOC) has been shown to influence the solubility and bioavailability of THg and MeHg in environments outside the Everglades, DOC has not been a major focus of research in the Everglades.

Eight locations, varying in chemical and biological characteristics, within the Everglades Protection Area (EvPA) were periodically monitored from 2011-2017 for water, floc, and biotic concentrations of THg and MeHg, along with ancillary chemical parameters in the surface waters (SUVA254 [specific UV absorbance at 254 nm], spectral slope between 275 and 295 nm [S275-295], and DOC, sulfate, sulfide, iron, phosphorus concentrations). Bivariate linear regression and multivariate (Principal Component Analysis) statistics indicated that DOC (range of 13 to 57 mg/L) and dissolved THg concentrations were most closely associated with the dissolved MeHg concentrations in water. With one exception, water MeHg concentrations increased with aqueous DOC concentrations across multiple sites; concomitantly, bioconcentration factors for periphyton decreased. The SUVA254 (a measure of the aromaticity of the DOC) was not related to aqueous MeHg concentrations across sites, but SUVA254 did show a positive linear relationship at one site dominated by invasive cattail (Typha) and Chara. Importantly, the slopes of trophic MeHg magnification throughout the food chain showed no relationship with DOC, or variation among sites. This suggests that spatial and temporal Hg variations in the upper trophic levels, such as in Gambusia, are primarily defined at the base of the food web, and that DOC may limit uptake of Hg particularly by basal food organisms.

Our data demonstrate that MeHg concentrations in the water column and biota are frequently higher at locations where the sulfate levels are ≤ 0.2 mg/L than in areas where sulfate consistently average between 15 and 32 mg/L. This suggests that sulfate reduction is not the only Hg methylation process operating in the Everglades, and that DOC acts to mediate the bioavailability of Hg and MeHg. Because DOC plays such a critical role in the uptake and bioaccumulation of MeHg in the food chain, investigations into the specific DOC structure and composition that influence the production of MeHg and its biological uptake should be pursued. This will assist in explaining why some areas of the Everglades are consistent Hg “hotspots”.

TP-066

BIOACCUMULATION OF METHYLMERCURY IN LARGEMOUTH BASS FROM MISSOURI FARM PONDS

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Bioaccumulation of methylmercury in aquatic food chains has led to national and state consumption advisories for many fish species. Atmospheric inorganic mercury deposited in bodies of water is converted to methylmercury by anaerobic sulfur-reducing bacteria. Through bioaccumulation, methylmercury levels trend higher in fish that are larger, at a high trophic level, with greater longevity. Mercury sequestration by plants may decrease availability for methylation and thereby reduce rates of bioaccumulation.

Here we report mercury levels in largemouth bass collected from 4 farm ponds in Daviess County, in the northwest region of Missouri, USA. The county is primarily agricultural and does not contain large urban areas; however, the significant number of coal-fired power plants in eastern Kansas and western Missouri may influence mercury deposition in this region. Fish lengths and weights were recorded and muscle samples frozen for determination of total mercury on a Teledyne Leeman Labs Hydra IIC Hg Analyzer. Fish lengths (cm) varied from 18.1 to 39.9. Total mercury (ng/g, wet weight) varied from 182 to 567. Additionally, DOC, alkalinity, cation concentration, anion concentration, and mercury concentration were measured in the associated water samples. Plant samples were separated into root, rhizome, and leaf sections, dried, and homogenized samples were analyzed for total mercury content.

The results show length and weight are highly correlated and thus either measure can be used when looking for gross trends in mercury accumulation. Largemouth bass above 10 inches in length (25 cm) contained mercury concentrations above the EPA limit of 300 ng/g. Based on a linear regression of data from all four ponds, variation in length explains most of the variation in mercury concentration. Pooling largemouth bass data from this year with similar work from previous years suggested that submerged aquatic vegetation (Potamogeton epiydrus - pondweed) might play a role in reducing bioaccumulation through mercury sequestration. Mercury concentration in the pondweed leaves was several orders of magnitude greater than in corresponding water samples, supporting sequestration by the plant material.

TP-067

MERCURY CHEMICAL FORMS IN AMAZON WATERS: BLACK, WHITE AND CLEAR

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Waters in the Amazon Basin can be classified by its optical characteristics as "black", "clear" and "white" with distinct physic-chemical properties defining aquatic environments. We studied total Hg (THg) methyl-Hg (MeHg) in water (W), suspended sediment (SSed), sediment (Sed), phytoplankton (P-plankton), Zooplankton (Z-plankton) and macro-invertebrates (Mac-Inv) in the three types of water found in the Madeira River Basin. The highest average concentrations of THg and MeHg were respectively 2.4ng.L-1, 0.43 ng.L-1 (black-W); 2.23 ng.L-1, 0.33 ng.L-1 (white-W); 2.2 ng.L-1, 0.31 ng.L-1 (clear-W). Average concentrations of THg in SSed were respectively 159.27 µg.Kg-1 (white-W); 122.39 µg.kg-1 (clear-W) and 107.16 µg.kg-1 (black-W). The average concentrations of THg and MeHg in Sed were respectively 77.5 µg.Kg-1, 0.44 µg.Kg-1 (black-W); 76.41 µg.kg-1, 0.33 µg.kg-1 (clear-W); 55.33 µg.kg-1, 0.24 µg.kg-1 (white-W). For P-plankton, average concentrations were respectively 322.35 µgKg-1, 19.2 µgKg-1 (black-W); 274.6 µg.kg -1, 12.9 µg.kg-1 (clear-W); 211.6 µg.kg-1, 9.4 µg.kg-1 (white-W). Z-plankton average of THg and MeHg concentrations were respectively 388.15 µgKg-1, 24.6 µgKg-1 (black-W); 333.87 µg.kg-1, 15.94 µg.kg-1 (clear-W); 246.34 µg.kg-1, 11.43 µg.kg-1 (white-W). The mean THg and MeHg concentrations in Mac-Inv were 701.39 µg kg-1, 65.8 µg.kg-1 (black-W); 636.91 µg.kg-1, 44.38 µg.kg-1 (light-W) and 645.73 µg.kg-1, 36.74 µg.kg-1 (white-W). Mean THg concentrations of Mac-Inv were not significantly different between the analyzed matrices. However, MeHg was significantly different between the analyzed matrices. The correlations between variables (W, SSed, Sed, P-plankton, Z-plankton and Mac-Inv) were more significant in the white-W, suggesting a greater connectivity of aquatic communities with geological environment. Correlations among biological variables (Phy, Zoo and Mic-Inv) were statistically significant in all three types of water suggesting an undiscernible pattern of biomagnification in these water ecosystems.

TP-069

EFFECTS OF MOLECULAR SIZE FRACTION OF DOM ON PHOTODEGRADATION OF METHYLMERCURY IN WATER

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This study investigated the photo-degradation kinetics of MeHg in the presence of various size fractions of dissolved organic matter (DOM) with MW<3.5 kDa, 3.510 kDa. The DOM fraction with MW<3.5 kDa was most effective in MeHg photo- degradation. Increasing UV intensity resulted in the increase of photodegradation rate of the MeHg in all size of DOM fractions. Higher rates of MeHg degradation was observed at higher pH values. For the portion of MW<3.5 kDa, the photo-degradation rate of MeHg increased with increasing DOM concentration, indicating that radicals such as singlet oxygen (1O2) radicals can be effectively produced by DOM. At higher portion of MW>3.5 kDa, the inhibition of MeHg degradation was observed due to the photo-attenuation effect. Our result indicates that radical mediated reaction is the main mechanism of photodegradation of MeHg especially in the presence of MW<3.5 kDa. Our results imply that the smallest molecular weight fractions (MW<3.5 kDa) of DOM mainly increased the photodegradation rate of MeHg.This study investigated the photo-degradation kinetics of MeHg in the presence of various size fractions of dissolved organic matter (DOM) with MW<3.5 kDa, 3.510 kDa. The DOM fraction with MW<3.5 kDa was most effective in MeHg photo- degradation. Increasing UV intensity resulted in the increase of photodegradation rate of the MeHg in all size of DOM fractions. Higher rates of MeHg degradation was observed at higher pH values. For the portion of MW<3.5 kDa, the photo-degradation rate of MeHg increased with increasing DOM concentration, indicating that radicals such as singlet oxygen (1O2) radicals can be effectively produced by DOM. At higher portion of MW>3.5 kDa, the inhibition of MeHg degradation was observed due to the photo-attenuation effect. Our result indicates that radical mediated reaction is the main mechanism of photodegradation of MeHg especially in the presence of MW<3.5 kDa. Our results imply that the smallest molecular weight fractions (MW<3.5 kDa) of DOM mainly increased the photodegradation rate of MeHg.

TP-070

MERCURY BIOAVAILABILITY FOR METHYLATION DECLINES RAPIDLY AFTER DEPOSITION TO SEDIMENTS

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The METAALICUS study, a whole-watershed mercury (Hg) addition experiment, was designed to evaluate the response of the Lake 658 ecosystem to changing Hg loads. In this paper, we examine the availability of Hg for methylation in sediments over 12 years, following 7 years of a whole-lake enriched stable isotope spike and 5 years of recovery. We compare MeHg production from the lake spike with

MeHg formed from native Hg in lake sediments. In surface (0-2 cm) sediments, the bioavailability of Hg for methylation declined rapidly after deposition to sediments. In the first year of lake spike additions, roughly 20% of Hgspike newly deposited to sediments accumulated as MeHg, compared to 3% of native Hg (which had an average age of about 14 years). The spike %MeHg dropped exponentially over the first 3 years of lake Hg additions, to an asymptote of about roughly 3-4%, similar to native MeHg. Sediment:water partitioning of spike Hg was an order of magnitude below that for native Hg in year one, rising to match native Hg after about 3 years. We conclude that the early sediment diagenesis into more recalcitrant phases (rather than burial) reduces the availability of sediment Hg for methylation with a decay half time of a few months. However, it did not decline to zero with the time period measured.

The absolute concentrations of spike Hg and MeHg in surface (0-2 cm) sediments rose during the 7 years of spiking, following the accumulation of loading. After spiking stopped, spike Hg and MeHg concentrations in surface sediments and pore waters declined, lessening the contribution of the spike Hg to overall MeHg production. However, there were low levels of ongoing spike Hg methylation for a decade, perhaps due to recycling of sediment Hg. These were reflected in low levels of lake spike MeHg in anoxic bottom waters, and in the lower food web, even several years after the spike stopped. These results strengthen our original METAALICUS conclusion that lakes can respond rapidly to decreases in direct Hg loading. However, the rate of response among lakes may vary with the rate of sedimentation. For example, if Hg deposited to sediments within the last year or two is a small fraction of the overall Hg pool in microbially-active surface sediments, the contribution of older, less-available Hg to overall MeHg production could be significant.

TP-071

DETERMINING THE EXTENT, RATE AND MECHANISMS OF MERCURY RELEASE FROM CONTAMINATED STREAMBANK DETERMINING THE EXTENT, RATE AND MECHANISMS OF MERCURY RELEASE FROM CONTAMINATED STREAMBANK SOILS

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During a period of mercury use in the 1950s and 1960s, large quantities of mercury were released to the headwaters of East Fork Poplar Creek (EFPC), a freshwater stream in Oak Ridge, Tennessee, resulting in elevated mercury concentrations in downstream soils, sediments, and biota. Mercury-contaminated soils are eroding into the stream, providing a potential source for conversion to methylmercury and bioaccumulation in the food chain. Our goal was to understand the extent, rate, and mechanisms of geochemical releases of mercury from EFPC bank soils. A series of equilibrium and kinetic batch experiments were conducted using EFPC water, water from an uncontaminated analogue stream, artificial creek water (ACW) with solution chemistry similar to EFPC, and ACW with 1 mg/L Sewannee River natural organic matter. Experiments were conducted with bulk soils at varying solid:water ratios (w/vol 1:5, 1:10, 1:30, 1:50, 1:100, 1:500, 1:1000) in ACW using a reaction time of 6 hours. Experiments were conducted using different soil particle size fractions (<0.053, 0.053-0.125, 0.125-1.00, 1.00-2.36, >2.36 mm) and all four water chemistries. High resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) were used to determine the form of mercury in the soils. In the near future, selective extraction will be used to estimate the extent of mercury release using 5 increasingly strong reagents.

The extent of mercury release increased until 12 hours, then decreased, and finally plateaued until the end of the experiment at 170 hours. Solid:water ratios up to 1:50 increased the extent of mercury release, but above this threshold, mercury release was invariant. At a 1:30 ratio, after 6 hours reaction time, and with size fraction 0.125-1.00 mm, the soils released from 0.001% to 0.05% of the original concentration of mercury, which ranged from 0.002 to 0.55 µg/L. SEM/HRTEM/EDS analyses suggested that mercury was present as mercury sulfides. After the solutions were reacted with the soils, the solutions were analyzed for major anions, cations, pH, specific UV absorbance at 254 nm, and dissolved organic carbon. Geochemical modeling will be used to predict the extent of dissolution using the equilibrium solution chemistry. Preliminary SEM/HRTEM/TEM results suggest that mercury was present as mercury sulfide, indicating the major mechanism of release is dissolution. Our results suggest that eroding bank soils could contribute substantial mass of Hg to EFPC waters, and thereby provide a source for mercury methylation in the creek.

TP-072

METHYLMERCURY PRODUCTION IN SURFACE SEDIMENTS AND EXCHANGES WITH OVERLYING WATER OF LAKE TITICACA (BOLIVIA)

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Lake sediments are an important source of the neurotoxic monomethylmercury (MMHg) for surface water, in which trophic transfer occurs in both benthic and pelagic organisms. Geochemical processes involved in mercury (Hg) methylation generally occur in surface sediments and imply various micro-organisms amongst which the most documented are sulfate reducing (SRB), methanogens and iron-reducing (IRB) bacteria. The goal of the present study was to improve our understanding regarding the fate and behavior of post-depositional Hg in the sediments of the high-altitude Lake Titicaca (3809 m a.s.l., Bolivia). Vertical profiles from six cores representative of the various sediment facies and ecological repartition were analyzed in high-resolution (5 to 10 mm-scale) for filtered and particulate Hg species (Hg and MMHg) together with redox-sensitive elements (N-species, Mn, Fe and SO42-) to evaluate the influence of early diagenetic processes on Hg interconversion and partitioning between porewater (PW) and sediment.

Our results highlight that the highest MMHg concentrations are found in surface sediment PW located in shallow (0 to 10m) and very shallow (0 to 2m) sites (5.8 ± 5.6 ng L-1) with MMHgPW rising up to 12.2 ng L-1 in top sediment covered by epibenthic biofilms while lowest MMHgPW were encountered in the deep (40m) lake sediments (0.84 ± 0.23 ng L-1). In particular, highest MMHg is encountered in the shallow carbonate facies sites where the low sediment OM and the high sulfate contents in both sediment and water (~ 250 mg L-1) are likely the major fuel for Hg methylation by SRB - the main Hg methylators in such environments. A striking feature of our results is the very elevated percentage MMHg encountered in almost all sites standing at 47 ± 26 % in very shallow, 39 ± 27 % in shallow sites and 23 ± 15 % in deeper sites.

Finally, calculated diffusive fluxes to the overlying water (e.g., 104 ± 16 ng.m-2.d-1 and 12 ± 8 ng.m-2.d-1 for carbonate facies and organic facies sediments, respectively) are compared with benthic chamber flux measurements performed in situ to evaluate diurnal and site-specific variability.

TP-074

UNCERTAINTY ANALYSIS FOR A MERCURY CYCLING MODEL USING THE MARKOV CHAIN MONTE CARLO (MCMC) BAYESIAN APPROACH

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A mathematical model was developed to predict mercury (Hg) concentrations for lakes in the Upper Peninsula (UP) of Michigan to help further understand the cycling of Hg. Several Hg models have been published but few have been evaluated for uncertainty in predictions. Models are often over-parameterized with up to 70 coefficients, few being constrained by measurements. These parameters are often lake-specific and cannot be generalized for all lakes. To address this problem, the UP is used as the location for this analysis because this region has many lakes, but many variables remain constant (e.g., latitude, land cover, deposition).

The model was developed in R and incorporates a mass balance for three Hg species (elemental, divalent, and methyl) in three compartments (epilimnion, hypolimnion, and sediments). It considers seasonality such as temperature, stratification, photolysis, ice cover, hydrology, and solids concentrations. Kinetics integrated into the mass balances include redox reactions, methylation, demethylation, photodemethylation, and partitioning. The model was calibrated, and sensitivity and uncertainty analyses were performed. Calibration consisted of comparing model predictions with lake measurements. For sensitivity analysis, model parameters were changed by a fixed percentage and changes in model predictions were compared. This presentation focuses on uncertainty analysis using a Markov Chain Monte Carlo (MCMC) Bayesian approach. This approach is based on Bayes Rule, where the posterior distribution of a parameter, given the dependent variable and fixed model data, is proportional to the likelihood function multiplied by the prior distribution. The prior distribution of parameters is obtained by compiling values cited in literature. In the MCMC approach, the model is run thousands of times to converge to the posterior distribution, and the estimate for each parameter is defined by the posterior mean.

The goal for this project is to use the model to understand sources of variability among lakes and to predict regional Hg storage and emission from lakes. Multivariate statistics and model scenario analysis are used to examine the sources of variability. Results from this statistical approach have shown the importance of the pH and DOC on Hg cycling in lakes; model scenarios suggest that seasonal ice cover influences methylmercury concentrations. Regional-scale estimation applies posterior distributions of parameters from the uncertainty analysis to groups of lakes having similar characteristics (size, mixing regime, trophic state). The combination of these approaches reveals some fallacies in common assumptions.

TP-075

STAYING FAR FROM THE SUN: HOW HELIOBACTERIA REDUCE MERCURY IN THE DARK

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Mercury (Hg) is a global pollutant that severely impacts ecosystem and human health when it bioaccumulates as methylmercury (MeHg). MeHg production is mediated by microbes that thrive in the absence of oxygen, as such, there is a growing need to understand the processes that affect Hg availability in anaerobic environments. Hg redox cycling is a key pathway that determines the amount of substrate HgII or Hg0 available for methylation. To date, the majority of work has focussed on Hg redox cycling performed by chemotrophic bacteria in aerobic environments, with the role of anaerobes and phototrophs having gone largely overlooked. Recently, weve shown that anoxygenic phototrophic purple bacteria contribute to Hg redox cycling when excess reducing power is available (in the presence of light and reduced carbon), however, whether such pathways occur in other anaerobes and/or phototrophs remains elusive. Our objective was to test whether similar Hg redox cycling pathways were present in a representative of the family Heliobacteria, Heliobacterium modesticaldum Ice1, capable of phototrophic and fermentative growth. We found that H. modesticaldum can perform Hg redox cycling during phototrophic growth, but discovered that it can also do so during fermentatively.

We determined that Hg redox cycling during fermentation depends on the availability of reduced cofactors and demonstrate that this pathway may be widespread in other anaerobes possessing a similar chemotrophic metabolism.

TP-076

SEASONAL PATTERNS IN MERCURY DYNAMICS AT THE BASE OF TWO CONTRASTING BOREAL LAKE FOOD WEBS

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There has been a rising trend in the amount of mercury (Hg) found in freshwater fish in northern lake ecosystems. In particular, climate change may lead to increased mobility of Hg by increased fluxes of dissolved organic carbon (DOC) associated with Hg to surface waters. The concentration of mercury in fish is thought to be strongly driven by processes at the base of the food web, where there are knowledge gaps and a great deal of variability in the degree of Hg accumulation.

Here, we present the result of a detailed seasonal study of Hg in the lower food web of two boreal lakes in southern Norway that have contrasting levels of DOC. Water and food web samples were taken from Røysjø (clear water lake) and Store Øyvannet (brown water lake). We tested out possible explanatory driving factors for Hg in aquatic food webs, in order to better be able to make predictions on concentrations and uptake and transfer of Hg through the food web. Analysis was carried out for a comprehensive set of samples taken during spring, summer and fall of 2016. Measurements of water quality, DOC and Hg were paired with the characterization of the base of the food web and trophic interactions based on stable isotope analysis in order to describe Hg trophodynamics.

We found that Hg concentrations in water from Store Øyvannet (the brown water lake) were approximately three-fold higher compared to Røysjø, highlighting the importance of organic carbon content as a factor for the Hg concentration in water. We saw seasonal patterns in Hg in both water and zooplankton. Methyl mercury (MeHg) concentrations tended to increase with increasing zooplankton size (the zooplankton was size fractionated). There was a significant difference in MeHg concentration in zooplankton (in the 200-500 micrometer size range) between lakes, with concentrations in Store Øyvannet approximately five-fold higher than in Røysjø. These data provide important insight into seasonal MeHg cycling in the lower food web of two contrasting lakes, and the effects of water chemistry and trophic interactions on MeHg concentrations in zooplankton.

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TP-077

METHYLMERCURY AND DOM: IMPLICATIONS FOR MERCURY CONTAMINATION

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Methylmercury (MeHg) bioaccumulation in biota is a serious concern for some remote ecosystems in Southwestern Nova Scotia. Sources of mercury to this area are both natural and anthropogenic, including bedrock and atmospheric deposition. While much is known about mercury methylation in freshwater, much less is known about demethylation. The loss of MeHg from water columns of lakes is dependent on several processes including adsorption, deposition to sediments, and demethylation. Microbial demethylation in lake water columns is very slow. Therefore, daytime photodemethylation facilitated by solar radiation can dominate MeHg removal from the water column. To better quantify the photodemethylation potential within lakes we must determine a) the variation in photoreactive compounds such as dissolved organic matter (DOM) and iron (Fe) and b) the availability of solar radiation with depth in water columns. Freshwater lakes were chosen in Kejimkujik National Park (44.23°N, 64.13°W) to include a wide range in dissolved organic carbon (DOC) and Fe concentrations. Water samples were collected over 3 years and analyzed for ultraviolet (UV)-visible absorbance, DOC, dissolved ions, total mercury, and MeHg concentrations. Floating sensors for UV, photosynthetically active radiation (PAR), and temperature were installed in two lakes of contrasting DOC concentrations. The depth of 95% UV attenuation was 40-50 cm in the lower carbon lake compared to 10-20 cm in the higher carbon lake. The effect of rainfall on UV attenuation was also less in the lower carbon lake compared to the higher carbon lake, most likely due to a difference in catchment area. Seasonal alterations to the solar angle of incident radiation strongly controlled the amount of solar radiation entering lake water surfaces and therefore outlined a possible photoreactive season or period within each year. These observations suggest that photodemethylation of methylmercury in lake water columns may be limited to a short period of approximately 4 months a year at 44°N. Overall, these field observations provide fine resolution solar radiation data and excellent temporal resolution over 3 years for mercury and carbon cycling.

TP-078

PREDICTION OF METHYLMERCURY PHOTODEMETHYLATION IN FRESHWATER LAKES

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Methylmercury (MeHg) toxicity is of particular interest in remote Canadian environments, far from point sources of contamination, where high levels of MeHg are accumulating in top predators. The ecosystem variables that control this sensitivity of food webs are not well known. MeHg concentration in water and uptake into the base of the food web is one key factor controlling mercury entry into food webs. Few studies have directly considered photodemethylation reactions in combination with physical attributes of aquatic ecosystems to predict where and when dissolved MeHg may be available. To address this research gap we have used numerous controlled and semi-controlled experiments that focused primarily on the quantification of the relationships between solar radiation exposures, dissolved organic matter (DOM), and MeHg within six freshwater lake systems in Kejimkujik National Park and National Historic Site in southwestern Nova Scotia. To better quantify the photodemethylation potential within these lakes we determined a) the behaviour of photoreactive compounds and b) the availability of solar radiation with depth in water columns. Experimental treatments were 1-week long in summer and fall and were exposed to natural solar radiation over that time period. Using these experimental outcomes coupled with field measurements of solar radiation availability within lake water columns, we have developed a model for predicting photodemethylation potential and efficiency within the top 1 m3 in oligotrophic dystrophic temperate lakes. These predictive results were then scaled up and used to calculate the overall photodemethylation potential in each of our six study lakes for comparison with MeHg concentrations in the corresponding food webs. This model may be appropriate for other aquatic ecosystems by simple standardization techniques depending on water quality characteristics such as DOM photoreactivity (structure), pH, and dissolved ionic species. Overall, this body of work yielded a method for predicting mercury availability to food webs depending on environmental and physicochemical factors. Climate change in temperate and boreal regions of Atlantic Canada is projected to increase rainfall amounts and occurrences and thus lead to browning of freshwaters and further inhibition to the photodemethylation pathway of MeHg reduction.

TP-079

IMPACT OF SEDIMENT CHEMISTRY AND SOLID-PHASE MERCURY SPECIATION ON MERCURY BIOAVAILABILITY IN THE ST. LOUIS RIVER ESTUARY

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The St. Louis River Estuary (SLRE) is a highly utilized recreational shallow (1-3m) freshwater estuary at the mouth of the largest tributary to Lake Superior. Fish and other aquatic biota in the estuary often contain high levels of methylmercury (MeHg) compared to the upstream river or Lake Superior. The upstream river is heavily impacted by mining sulfate loads in a watershed dominated by atmospheric mercury depositions from regional and global sources. The downstream estuarine area contains some high mercury legacy sediment contamination from previous industrial activities, contributing to the listing of the SLRE by the EPA as one of 27 Areas of Concern in the Great Lakes region. Legacy contamination, water and sediment chemistry, and wetland area abundance in the estuary have all been presented as possible contributors to differences in mercury mobility and bioavailability as well as methylmercury production. In this study, we focus on the impact of sediment chemistry and solid-phase mercury speciation on inorganic- and methyl-mercury bioavailability and partitioning in relation methylmercury production in the estuary. Sediment cores and porewater were collected from five geochemically distinct locations within the estuary and analyzed for total and methylmercury, carbon (solid and porewater), and AVS/SEM or dissolved sulfide. In addition, selective extractions were used to separate solid phase mercury compounds into behavioral classes. Initial results indicate legacy mercury contamination does exist in some locations (at an order of magnitude higher than unaffected sediments), primarily in the lower harbor. Methylmercury production was highest in sediments with intermediate organic carbon content (around 10% LOI), however porewater total mercury was negatively correlated to organic carbon. Also, methylmercury production and porewater methylmercury was lowest in sediment with the highest sulfide, suggesting both inorganic and methylmercury availability are partially controlled by solid phase organic carbon and sulfate. Selective extraction results help to elucidate the solid phases involved in binding mercury, separating the solid-phase mercury present into water soluble, stomach acid soluble, organo-chelated, elemental, and mercuric sulfide classes. Coupled with total and methylmercury data, selective extraction results allow for the assessment of bioavailable mercury pools throughout the SLRE.

TP-080

CYANOBACTERIA AS REGULATORS OF METHYLMERCURY PRODUCTION IN PERIPHYTON

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Biotic methylation of Hg appears to depend on factors such as microbial activity and the concentration and bioavailability of Hg to the methylating organisms. Recently, the possible relationship between cyanobacteria and the production of methylmercury (MeHg) has been suggested. In this sense, this work aims to test in microcosms the net MeHg production in relation to the concentrations of periphytic cyanobacteria, DOC, phosphorus and primary periphytic production rates. We collected water and samples of periphyton for cultivation and isolation of cyanobacteria in floodplain environments of the Guapor River Wetland (Amazonia, Brazil). Periphyton was cultivated in microcosms with different concentrations of wild local cyanobacteria (n=30), total phosphorus (n=15) and natural local DOC (n=15). Tests of net mercury methylation potentials were done in incubations with local water and samples of the microcosms, using 203HgCl2 as a tracer. The primary periphytic production was evaluated by the oxigen production in light and dark bottles. Incubations with commercial cyanobacterial crops were also conducted. The highest net MeHg production occurred in the microcosm with the addition of wild cyanobacteria (7 to 25%), followed by microcosms with phosphorus addition (6 and 11%) and DOC (6 and 9%). There was no significant Hg methylation in incubations with commercial crops. In our experiments, there was a positive correlation between the production of MeHg, additions of cyanobacteria (R2= 0.694; p=0.001), phosphorus (R2= 0.521; p=0.04), DOC (r2= 0.611; p=0.001) and periphytic primary productivity. Our results point to two new possible predictors of Hg net methylation potentials: i) periphytic primary productivity, and ii) cyanobacterial concentrations in the periphyton. We hypothesized that the participation of these variables are due to the increase in energy resources (mainly H) for communities of Hg-methylating bacteria.

TP-081

THE TWIN CRATER LAKES OF NEWBERRY VOLCANO, OR: TWO LAKES, TWO POISONS

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The Newberry volcano crater lakes near Bend, Oregon, are small, seasonally mixed twin lakes filled with carbonate-rich, meteoric waters at ambient temperatures. East Lake (EL) has a pH of 6.5-7, 65 ppm SO4, and an active geothermal-volcanic CO2 + H2S input at its lake bottom. The diffusive CO2 flux into the atmosphere of ~50 tonnes CO2 /day is presumably similar to the geothermal gas input rate. EL fish have Hg contents 0.5-3 ppm Hg, and the sediment, with ~ 10% Corg, has up to 4 ppm Hg. Elemental Hg gas enters at the lake bottom with the geothermal gas flows, and bottom waters have 1.0 - 3.3 picomolar Hg(o). The Hg(o) is oxidized to Hg2+ in the water column, which then is probably methylated by sulfate-reducing bacteria. This methylated Hg is then taken up by diatoms and other algae, and accumulates in the sediment at a rate of ~5 kg Hg/year. Elemental Hg gas may leave the lake surface as well, where we find ~ 1.8 picomolar Hg (o) in the water. The combined input of Hg and sulfur makes for a perfect Hg methylation storm in EL. Paulina Lake (PL) is separated by a < 1 mile wide volcanic ridge from EL, and has no free CO2 bubbles, has more carbonate-rich waters devoid of SO4, and has a pH ~8. PL sediment has <50 ppb Hg and its fish carry <0.1 ppm Hg. PL has up to 250 ppm As and up to 14 % Fe2O3 in its sediment, and ~ 15 ppb As in the water column. EL on the other hand is virtually free of As, and its sediment has < 2% Fe2O3. We conclude that a phase separation at depth in the geothermal fluids leads to a largely gaseous input with Hg into EL; the residual degassed geothermal fluids enter PL, carrying abundant Si, As, P, and Fe. Some PL sediment contains 10 % of the diagenetic mineral vivianite (Fe-phosphate), a potential host for the As. The sediment of both lakes consists largely of biogenic silica (diatoms), ~ 10 % silicic volcanic ash, Corg, with an additional Fe-rich hydrothermal component at PL. The two lakes have existed ~ 8000 years suggesting a lifetime accumulation of 40 tonnes Hg in the EL sediment column. Future work involves a study of the methylation process in EL and potential Hg fluxing from its surface.

TP-082

MERCURY AND METHYLMERCURY YIELDS FROM RIVERS IN NORTHERN MINNESOTA, USA

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To reduce mercury in fish, Minnesotas Statewide Mercury Total Maximum Daily Load study set a goal for Hg emissions reductions. To potentially inform additional mitigation, studies are underway to better understand processes governing mercury bioavailability in aquatic food webs. Here we present initial results of load monitoring of Hg and MeHg, along with ancillary analytes, for seven northern Minnesota rivers. Two years of load monitoring are presented for four of the rivers and one year for the others. In addition to the most downstream station on all rivers, four rivers had a sub-watershed station, and one river was monitored at ten sub-watershed stations. Flow gages provided mean daily discharges and were maintained by the interagency Cooperative Stream Gaging Program. Water sampling usually began after ice out (March-April) and continued through October, acquiring 15-25 samples during that period. The rivers are distinctly different in their mix of land cover (ranging from 5 to 89 percent forest/wetlands) and water chemistry (e.g., sulfate, total organic carbon, and suspended solids). Total organic carbon concentrations ranged from 5.7 to 33 mg/L (medians: 9.3 21.3mg/L). Sulfate concentrations ranged from 0.57 to 1800 mg/L (medians: 1.1 697.3 mg/L). Rivers with the highest MeHg concentrations showed a stronger response (steeper slope) to water temperature. Annual yields ranged from 0.327 2.59 g/km2 for total Hg and 0.011 0.206 g/km2 for MeHg. Yields for Hg and MeHg were strongly correlated to TOC yields (R2: 0.85 and 0.84). The positive relationships between TOC and Hg and MeHg were much stronger in terms of yield than concentration. There were no significant relationships between yields of Hg, MeHg, sulfate, and suspended solids. An additional year of load monitoring for the rivers with only one year will complete this part of a larger study of mercury bioavailability. The final product of this study (ca 2018) will compare results from co-occurring studies of mercury methylation and food web biomagnification.

TP-083

MERCURY METHYLATION AND DEMETHYLATION ACROSS DIFFERENT RIPARIAN LANDSCAPES

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Through water quality and fish monitoring across Minnesota watersheds, five rivers have been identified to have particularly elevated mercury concentrations in fish despite relatively low total mercury concentrations in water and sediment. One hypothesis for these "high-five" rivers is that methylmercury production in riparian areas and the hydrological connectivity of riparian areas to streams in these five watersheds are important contributors to river methylmercury loads and bioaccumulation. To test this hypothesis, we conducted methylation (k-meth) and demethylation (k-demeth) assays, using enriched mercury isotopes, across two geomorphically distinct riparian zones in each of the five watersheds and across seasons from 2015 through 2016. Early analysis suggests that mercury methylation is enhanced in riparian areas within both wetland and agricultural landscapes versus riparian areas within forested landscapes. K-meth in riparian soils within agricultural and wetland environments are 0.014/d ± 0.011 and 0.013/d ± 0.010, respectively. Except for one study location, k-meth in riparian soils of forested landscapes are lower, 0.009/d ± 0.006. Methylmercury demethylation is similarly greatest in the wetland and agricultural riparian environments compared to forested riparian zones, although significant variability is observed. K-demeth values in soils from the agricultural, wetland, and forested riparian landscapes are 1.20/d ± 0.93, 1.51/d ± 1.37, 1.08/d ± 0.58, respectively. Our results suggest that both higher methylation and demethylation are positively related to areas that are more frequently inundated, such as in the agricultural and wetland landscapes. Riparian areas within forested regions may not contribute as much to riverine methylmercury because of lower inundation frequency and extent across these watersheds.

TP-084

METHYLMERCURY IN GREAT LAKES WATER, SESTON, AND BIOTA

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With the establishment of the Great Lakes Restoration Initiative in 2010 and an understanding that fish consumption advisories for mercury exist for all five of the Laurentian Great Lakes, the U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency (USEPA) initiated an effort to better understand mercury sources, cycling, and bioaccumulation. A significant motivation for this effort stemmed from the observation that while elevated fish mercury levels are well known, mercury monitoring and assessment efforts in the Great Lakes are relatively few, and no previous efforts have been conducted to systematically sample and analyze water, sediment, and lower trophic-level biota across the ecosystem. Starting in August, 2010, biannual (April and August) sampling surveys of water, seston, sediment, and benthos were conducted onboard the USEPA research vessel Lake Guardian. Seston (>63 um) was collected vertically with a plankton net towed through the epilimnion (20 m deep at most sites) to the surface. Surface water was simultaneously collected using Teflon-lined Niskin bottles mounted on a sampling rosette that were remotely triggered to collect water at key depths. Surficial sediments (top 2 cm) and Quagga mussels were collected with a Ponar dredge. Samples were analyzed for MeHg and dissolved organic carbon (DOC, waters only) at the USGS Mercury Research Laboratory.

Concentrations of MeHg (1.5 9.0 pg/L) and DOC (1.2 2.4 mg/L) in filter-passing water were extremely low, and increased from the upper to the lower Great Lakes following a general increasing trend of productivity and anthropogenic influence (SuperiorHuron>Michigan>Ontario>Erie) as productivity decreases and was negatively correlated with water and sediment MeHg. Clear seasonal differences for seston MeHg were also observed. April MeHg concentrations were approximately two times higher than August in all lakes except Erie, where April concentrations were half of August levels. Methylmercury concentrations in Quagga Mussels and Lake Trout (6.5 19.0 and 92 208 ng/g dry weight, respectively) were positively correlated with seston MeHg, suggesting that seston mercury drives foodweb concentrations. Seston-water MeHg partitioning (log-Kd) ranged from 5.4 to 7.0 L/kg and reflected both seasonal and between-lake trends observed for seston MeHg concentrations. We observed a negative relationship between water-seston MeHg partitioning and DOC, indicating that MeHg partitioning to DOC may limit MeHg uptake into the foodweb.

TP-085

INFLUENCE OF TIME DEPENDENT HG(II) REACTIVITY ON THE ESTIMATION OF METHYLATION AND DEMETHYLATION POTENTIALS

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Mercury (Hg) methylation and monomethylmercury (MMHg) demethylation activity of periphyton biofilms from East Fork Poplar Creek, a Hg impacted stream in East Tennessee, were measured throughout 2016 using stable Hg isotopic rate assays. To evaluate methylation/demethylation rate potentials, ^{201}Hg(II) and MM202Hg were added to structurally intact periphyton samples in ambient streamwater while the formation of MM^{201}Hg and loss of MM202Hg were monitored over time.

The data were modeled by simultaneously fitting first-order production (MM^{201}Hg) and decay (MM202Hg) equations to estimate methylation and demethylation potentials, respectively. Preliminary results indicated methylation rates were non-first order, resulting in poor model fits to the MMHg production data. This was hypothesized to be caused by the decreasing bioavailability of the ^{201}Hg(II) during the assay. Additional experiments approximated the change in ^{201}Hg(II) bioavailability during the assays by measuring both ^{201}Hg(II) sorption onto periphyton and the conversion of ^{201}Hg(II) to ^{201}Hg(0) over time after its addition to periphyton samples. Hg(II) sorption was well described by two-site first-order kinetic sorption. The data also suggested decreasing bioavailability of the MM202Hg over time which was approximated by measuring the rate of MM202Hg sorption. The MM202Hg sorption data were also well described by two-site first-order kinetic sorption. The model was extended to include the (i) Hg(II) sorption, (ii) Hg(0) production, and (iii) MMHg sorption as mechanisms contributing to the temporal decline in bioavailability. This new model yielded improved first-order fits to the methylation and demethylation data. Comparisons between our modelling method and more commonly used fitting techniques (e.g., the use of single time points to determine methylation and demethylation and fitting production and decay equations to methylation and demethylation data separately) are made.

TP-086

MONITORING OF MERCURY IN CATSKILL REGION FISH

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Catskill region of New York State, USA, was identified as one of the hotspots for mercury (Hg) bioaccumulation in gamefish in a 2008 study of 131 waterbodies within New York State (NYS). We reinvestigated from May to November 2016 13 waterbodies within the Catskills in collaboration with Syracuse University (SU) and the NYS Department of Environmental Conservation as part of the statewide monitoring program commissioned by the NYS Energy Research and Development Authority. A total of 277 individual fish were sampled from a pool of four frequently consumed gamefish species: *Sander vitreus* (Walleye), *Perca flavescens* (Yellow Perch), *Micropterus dolomieu* (Smallmouth Bass) and *Micropterus salmoides* (Largemouth Bass). Each fish was identified by species and measured for total length (mm) and weight (g), and a tissue sample was taken using an Acuderm® inc. 7mm acu-punch. Tissue samples were analyzed at SU for total mercury in solids using a Milestone DMA-80 in compliance with EPA method 7473. Nearly all (> 95%) of total Hg (THg) in fish is known to be methylmercury (MeHg); therefore THg served as a reasonable proxy for MeHg in fish. The highest THg concentrations were detected in Walleye (mean = 0.526 µg g^{-1} THg, standard deviation = 0.514), ranging 0.054 to 1.785 µg THg g^{-1} wet weight while yellow perch had the lowest mercury concentrations (mean = 0.187 µg g^{-1}, standard deviation = 0.174) and ranged from 0.016 to 0.911. Using Akaike's information criterion (AIC) model selection, we concluded that out of the three morphometric parameters and all possible combinations, the additive effects of species and length best explained the observed patterns in Hg concentrations in fish, while weight had minimal predictive utility. Further data analysis to evaluate the utility of water chemistry and geographical parameters in prediction of fish Hg is ongoing.

TP-087

MERCURY BINDING TO DOM PROBED BY AN E. COLI FLUORESCENT BIOREPORTER

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Mercury (Hg) assimilation by microbes in aquatic environments is an important step in bioaccumulation and bioconcentration in the food web. The inorganic dissolved mercury concentration available to microbes is strongly influenced by other ligands in solution, notably sulfur species and dissolved organic matter (DOM). In this work, we used the bacterial bioreporter, Escherichia coli HMS174 (pRB28/27) in an experimental study to assess the concentration of Hg2+ in the presence of 3 different DOM samples.

The three DOM samples that were used, include: Suwanee River NOM, primarily from a terrestrial blackwater source; Upper Mississippi River NOM, mainly a terrestrial-derived DOM; and Pony Lake fulvic acids isolated from an entirely microbial source. The patterns of mercury bioavailability were assessed in three different Hg and dissolved organic carbon (DOC) concentrations and statistically analyzed using linear regression and correlations to the DOM characteristics, including elemental composition, molecular structure, and optical properties through fluorescence 3D excitation emission matrices. Results indicated Hg bioavailability was most strongly correlated to the sulfur content of DOM, more specifically, the Hg:S ratios between 90 and 50 ng Hg mg-1 S ($r = -0.94$, $p = 0.22$). As the relative sulfur content of DOM increased, so did Hg binding to the DOM, likely attributable to the strong affinity Hg2+ has to sulfur functional groups.

TP-088

LONG-TERM INCREASES IN TOTAL ORGANIC CARBON AND TOTAL MERCURY CONCENTRATIONS IN A STREAM DRAINING A NORTHERN PEATLAND.

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Peatlands are hotspots of carbon and mercury (Hg) cycling, and have high concentrations of both solutes in outlet streams. Importantly, trends of increasing dissolved organic matter (DOM) concentrations have been found in streams for many northern catchments, which has been attributed to various drivers of environmental change. Since DOM and Hg cycling and transport are tightly coupled, it is important to determine if long-term increases in stream DOM concentrations are associated with changes to Hg transport in northern peatland ecosystems. The Marcell Experimental Forest (MEF) in forests of northern Minnesota (USA) was established during the 1960s to study the hydrology and ecology of catchments having upland soils that drain through central peatlands to streams that are headwaters of the Mississippi River and Hudson Bay. We show that annual volume-weighted concentrations of stream total organic carbon (TOC) and total mercury (THg) concentrations increased from 1993 to 2015. Over the same period, streamflow decreased. Stream THg concentration showed a weak positive correlation with TOC concentration and a weak negative correlation with streamflow. Likewise, interannual shifts in streamflow, TOC concentration, and THg concentration sometimes varied directions and relative magnitudes, suggesting complex underlying mechanisms. While suggestive of long-term changes in carbon cycling and Hg dynamics in peatland catchments, we urge caution in extrapolating these specific results for other sites where DOM concentrations have increased. Nonetheless, the long-term record may be the first documentation of THg concentrations that have increased in recent decades and that the increase has occurred over the same period as increases in TOC concentrations.

TP-089

MERCURY METHYLATION IN RESERVOIRS OF NORTHERN MANITOBA, CANADA: EFFECTS OF HYDROELECTRIC REGULATION AND CLIMATE CHANGE

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Since 1922, Manitoba has seen significant hydroelectric development with the opening of 15 hydroelectric reservoirs and the Churchill River Diversion which transports significant flow from the Churchill River to the developed Burntwood-Nelson River System, harnessing its power. Currently an average of 30 billion kilowatt hours per year are produced from the 15 operational hydroelectric reservoirs in Manitoba. Total mercury (THg) concentrations in fish are known to increase within 10 years of reservoir impoundment. Increases are thought to be temporary, with recovery to pre-impoundment concentrations generally occurring within a few decades. Over the last decade however, there has been an increasing trend in the fish mercury levels of both the regulated and unregulated reservoirs in Manitoba. In this study, we aim to quantify the contribution of hydroelectric regulation on the production of methyl mercury within an ecosystem with a rapidly changing climate.

As part of a larger interdisciplinary project to assess changes to the Hudson Bay System, we are addressing gaps in historical monitoring programs in the Hudson Bay watershed to incorporate controls on mercury cycling in aquatic systems. This is being achieved by providing meaningful seasonal results of sulfide, THg, methyl mercury and a more comprehensive characterization of the organic matter (OM) in the system. We have identified 4 key lakes, 2 regulated and 2 non-regulated, in the Churchill River Diversion and the Nelson River systems in northern Manitoba as field sites for determining the extent to which reservoir mercury cycling is impacted long-term by hydroelectric regulation.

Preliminary results from water column sulfide, THg, and methyl mercury concentrations in our field sites suggest that methylation in the systems in question is linked to sulfide production. During the studied seasons, THg, sulfide and MeHg concentrations differed amongst on system and off system reservoirs. Future analysis of OM and sediments will allow us to draw connections to mercury methylation and build upon relationships explored in experimental reservoirs.

TP-090

MERCURY IN A PRISTINE ANDEAN PATAGONIAN CATCHMENT (SOUTHERN VOLCANIC ZONE, ARGENTINA): SPECIES OCCURRENCE AND INTERACTION WITH DISSOLVED ORGANIC MATTER WITHIN A FLUVIAL NETWORK

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The mercury (Hg) transport within watersheds is regulated by water flux and hydrological paths, and coupled with the movement of dissolved organic matter (DOM) and particulate material. In Brazo Rincn (BR), a branch of Lake Nahuel Huapi (Northwestern Patagonia, Argentina), lake biota bear high Hg levels after the precipitation season, which is apparently related to volcanic activity in combination with high seasonal precipitation in the area (3500 mm y-1). We propose that these factors together with low DOM concentrations favor high Hg levels in the aquatic biota. We examined the occurrence of different Hg species (Total Hg, THg; Methyl Hg, MeHg and dissolved gaseous Hg, DGM) in the freshwater network draining to BR, applying Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). We analyzed the effect of DOM (concentration and quality), and suspended load (SL) as factors potentially influencing Hg speciation and partitioning. DOM concentration was estimated by dissolved organic carbon [DOC] and its quality through absorbance and fluorescence parameters. Chlorophyll a (Chla) was determined in the depth profile of BR. Overall, THg ranged between 41-363 ng L-1 in streams while in BR was higher in upper (114-268 ng L-1) than in deeper (16-36 ng L-1) strata. Particulate-THg and Filtered-THg ranged between 7-67 ng L-1and 15-304 ng L-1 in streams and 0.3-77 ng L-1 and 17-202 ng L-1 in BR. Estimated Hg2+ was higher in streams (40-362 ng L-1) compared to BR (17-263 ng L-1) in which upper layers showed higher concentrations. MeHg ranged between 0.01-0.3 ng L-1 in streams, and varied between 0.01-0.16 ng L-1 in BR, with higher concentrations in the upper strata. DGM was lower in streams (0.12-1.8 ng L-1) than in the water column of BR (0.1-7 ng L-1), with higher values up to 60 m, decreasing sharply towards the bottom. In general, our results suggest that the high but variable levels of different Hg species in streams and their positive relationship with terrestrial signatures of the DOM, reflect coupled inputs from the catchment and low effect of internal processing. Conversely, in the lake, different conditions are observed in the depth profile, indicating that internal processing (autochthonous production, photo- and biodegradation) operate concomitantly on DOM and Hg species to favor the production of DGM in the illuminated upper layers and binding of Hg to biological particles (phytoplankton), as suggested by the positive relationship Hg-Chla. Interestingly, in the streams Hg was mostly bound to inorganic particles.

TP-091

BIOLOGICAL AND GEOCHEMICAL CONTROLS OF MERCURY METHYLATION IN MEROMICTIC LAKES

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Production of methylmercury (MeHg) from ionic mercury (Hg2+) occurs largely in aquatic environments devoid of oxygen and nitrate (NO3-) such as, lake and estuarine sediments, wetlands, and anaerobic hypolimnia. Recent studies have found that methylation of Hg2+ is a result of the activity of hgcA and hgcB enzymes and confirmed the methylating capability of >70 microorganisms, thus unveiling potential new habitats for methylation.

We studied the transformation of mercury species and bacterial community structure in two meromictic lakes, Glacial Lake, Jamesville, NY and Green Lake, Fayetteville, NY. Meromictic lakes are stable anoxic basins with lower, euxinic stratum, which is permanently separated from an upper, well oxygenated stratum. The interface between the two strata (chemocline) is characterized with steep temperature, density, and geochemical gradients. Glacial Lake and Green Lake harbor rich microbial assemblages of phototrophic S bacteria (PSB), which likely process Hg but no phylogenetic or field study have been undertaken to confirm their involvement.

Samples were collected between 2014-2016. In situ field measurements were made for dissolved oxygen (DO), NO3-, sulfide (HS-), temperature, pH, specific conductance, turbidity, and chlorophyll a. Additional samples were collected for chemical (total Hg, MeHg, dissolved organic carbon, and bacterial chlorophyll) and microbiological (DNA sequencing, droplet PCR, and qPCR) analysis. Redox parameters delineated a spatially-wide zones of anoxic and anaerobic metabolism in both lakes, which followed the theoretical thermodynamic sequence of electron acceptors. Vertical distribution of total Hg and MeHg had distinct profiles with noteworthy peaks at the chemocline, associated with high turbidity and peaks in bacterial chlorophyll. Anoxygenic phototrophic bacteria comprised a sizable portion of the microbial community at the chemocline of both lakes. Droplet PCR and phylogenetic sequencing showed high abundance of purple PSBs (>50 % of total biomass) in the chemocline of Green Lake, while predominance of green PSBs (> 52% of total microorganisms sequenced) in Glacial Lake. Concentrations of the hgcA and hgcB genes reached maximum at the chemocline as well. Multiple lines of evidence suggest that anoxygenic phototrophic bacteria contribute to the enhanced methylation of Hg2+ at the chemocline.

TP-092

METHYLMERCURY HOTSPOTS AND CYCLING ACROSS TERRESTRIAL AND AQUATIC COMPARTMENTS OF A HIGH ARCTIC SUB-CATCHMENT

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Previous studies have found elevated levels of MeHg in certain Arctic freshwater fish, which are a staple in northern Aboriginal peoples diets. This raises environmental and human health concerns, highlighting the importance of understanding the spatial and seasonal variations in MeHg sources to freshwater ecosystems. This research aims to determine where hotspots for production (methylation) and degradation (demethylation) of MeHg occur in High Arctic landscapes. To address these objectives a series of field based experiments to quantify Hg methylation and MeHg demethylation, as well as spatiotemporal surveys of MeHg and total Hg concentrations, were conducted in the Skeleton Lake sub-catchment of Ellesmere Island, Nunavut, Canada. This sub-catchment allows us to track MeHg concentrations and production during downstream transport along a continuum from the permafrost seep headwaters, through Skeleton Lake, a series of shallow ponds, a wetland stream, a sedge meadow wetland and finally at the inflow of the creek into Lake Hazen. Thus, we are able to quantify how MeHg is transformed during downstream transport through various compartments of the catchment, particularly at the terrestrial-aquatic interface. Sampling and experiments were conducted during the ice-free, summer growing season of 2016. Hg methylation and MeHg demethylation were quantified using enriched stable isotope tracers in 1) the Skeleton Lake water column; 2) Skeleton Lake sediments; 3) downstream pond sediments; and 4) wetland soils, both along the stream and in the sedge meadow. A spatial survey was also conducted along the entire length of the wetland stream and meadow to quantify Hg and MeHg in wetland soils across the terrestrial-aquatic interface, and aqueous concentrations of MeHg and total Hg were measured weekly throughout the continuum. Preliminary data suggests that while there is net production of MeHg in the lake and pond sites, wetland soils act as a very important sink for MeHg, reducing its export into Lake Hazen. In spring 2017, additional methylation/demethylation measurements will be carried out in snowpacks, and in Skeleton Lake water, at a time persistent ice cover has led to the development of bottom water anoxia, thus providing ideal conditions to support the activity of anaerobic methylating microorganisms. This research will result in a better understanding as to where MeHg is produced and decomposed on the Arctic landscape as well as provide insight into seasonal patterns and differences in MeHg sources and cycling.

TP-094

METHYLMERCURY PHOTO-DEGRADATION RATES IN SURFACE WATERS OF THE SAN FRANCISCO BAY DELTA ESTUARY

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The photochemical degradation of methylmercury (MeHg) by sunlight is an important process which can influence MeHg concentrations and cycling in surface waters. We compared MeHg photo-degradation rates from surface waters of three rivers (Sacramento, Mokelumne, San Joaquin) with surface waters from freshwater wetlands (Yolo Wildlife Area) in the San Francisco Bay Delta Estuary (Delta), California, U.S.A. Photo-degradation rates were determined using in situ bottle and bag incubations, with incubation periods from a few hours to several days. PAR and UV photo-degradation rate constants (k, ng L-1 E-1 m2) were obtained by regressing MeHg concentrations obtained at different time periods against cumulative light intensity or total light exposure. PAR and UV photo-degradation rate constants were -0.0139 and -0.202 ng L-1 E-1 m2 respectively for Delta rivers and -0.0047 and -0.116 ng L-1 E-1 m2 respectively for Delta freshwater wetlands. An ANCOVA was used to test for the equality of slopes and showed that the photo-degradation rates (slopes) for the rivers and wetlands are significantly different. This suggests that the type of water body (e.g. Rivers vs wetlands) has significant influence on MeHg photo-degradation rates and hence MeHg concentrations. Consideration of the water type is therefore critical when developing models of photo-degradation of MeHg across the Delta. Water body specific MeHg photo-degradation rates may be required for accurate predictions as the Deltas physical make up includes arrays of large rivers, small tributaries, marshes, diked islands, and flooded tracts. Preliminary findings reveal that when integrated temporally and spatially, photo-degradation of MeHg is a dominant loss term for dissolved MeHg in the Delta, exceeding riverine export losses by over a factor of 3.

TP-095

CLIMATOLOGICAL DRIVERS OF METHYLMERCURY PRODUCTION IN A HIGH GRADIENT STREAM

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The South River is a high gradient stream located in central Virginia, USA that seasonally generates increased concentrations of methylmercury (MeHg) in surface water despite lacking geomorphological characteristics thought to favor methylation (e.g., wetlands). Concentrations of MeHg in surface water range from <0.1 to ~3 ng/L in the unfiltered fraction, and have a strong seasonal component. Analysis of the previous decade of data collected seasonally in the South River reveals that the proportion of total mercury (THg) as MeHg in surface water is predicted (multiple R2 = 0.78) by three factors the concentration of inorganic mercury (IHg), the surface water discharge and surface water temperature. This relationship is significant (ANOVA; $p<0.001$) over a wide range of temperatures and the concentration of IHg in both the filter-passing and particulate fractions; the relationship is observed in both upstream reference areas and downstream of the historical source, indicating that methylation rates are responding to increases in temperature in the river channel.

This finding has significant implications for the South River food web and responses to remediation. Larval aquatic organisms are exposed to MeHg on particles and in the colloidal (i.e., filter-passing) phases of surface water. The concentration of IHg in surface water, which is correlated with the concentration in sediment is therefore a critical indicator of MeHg exposure to the food web. Remedial solutions should focus on reducing the loading of new IHg to the system, which is likely methylated more rapidly than older IHg in the system based on results from other systems. Climate change and changes to the watershed (e.g., urbanization) that may affect surface water temperature could also affect microbial methylation rates. However, the relationship between methylation and temperature is not completely linear the highest MeHg concentrations are not necessarily observed during maximal surface water temperature. Future monitoring data on surface water will allow for more insight into how the South River might respond to perturbations including remediation, climate change and urbanization.

2e: Artisanal Small-scale Gold Mining (ASGM): Current and historical emissions, current practices and future projections

TP-097

MAPPING THE FATE OF QUICKSILVER: MERCURY CONTAMINATION FROM ARTISANAL GOLD MINING IN SENEGAL

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In developing countries across Asia, South America, and sub-Saharan Africa, mercury is utilized to isolate gold from sediment in artisanal mining, the largest anthropogenic source of mercury emissions. This mercury is then released into the environment either through local atmospheric emissions or as mining tailings, presenting a health risk for humans and biota. Though many studies have examined the health impacts of the mercury vapor, little is known about the fate of local mining waste, including the extent of contamination and its pathway of loss, especially in sub-Saharan Africa. In this study, we examine mercury from artisanal gold mining in southeastern Senegal. This region currently produces over 4 million tons of gold per year, while releasing over 5 tons of mercury into the atmosphere; these values are expected to increase in the future. We examine the ecological impact of artisanal gold mining using soil, water, and sediment samples collected from three mining communities to determine the pathway of mercury into the environment. We assess patterns in total mercury and methylmercury concentrations in huts where mercury is burned, piles of mine tailings, and along transects to the nearby streams. We utilize these patterns to gain insight into biotic and human exposure to mercury both in the mining villages and downstream communities. We will present data on the implications of this contamination for ecosystems.

TP-098

MERCURY CONTAMINATION IN ENVIRONMENTAL MEDIA FROM ARTISANAL SMALL GOLD MINING AREAS IN CENTRAL KALIMANTAN, INDONESIA AND HUMAN HEALTH RISK ASSESSMENT

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Mercury, the only liquid metal element at ambient temperature and pressure, has a low boiling point (357°C). Therefore, mercury evaporates easily at ambient conditions and is readily emitted from various sources. In 2010, the majority of global anthropogenic emissions of mercury to the atmosphere were associated with artisanal and small-scale gold mining (37.1 %).

One of the gold mining activity area in Barito river watershed is located in Mangkahui Village, Murung sub District, Murung Laya Regency which approximately 470 km apart from Palangkaraya city, the capital city of Central Kalimantan. Gold processing plants are located at the center of the Mangkahui Village. There were fifteen gold processing plants constructed along the main road in the village (within 500 m) which consists of 10 to 24 steel-made ball mills at every single processing plant which employees 30 to 40 workers.

Mercury concentration in atmosphere, water and soil were observed in the ASGM activity sites. We also observed the mercury concentration in fish and rice. Based on our field observation, we conducted human health risk assessment originated from ASGM activity. Health risk assessment was conducted by the Hazard Quotient (HQ) and Hazard Index(HI) which is provided by the US EPA.

TP-099

MERCURY POLLUTION AND ITS RISK ORIGINATED FROM THE ASGM MINING ACTIVITY IN MONGOLIA

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Exposure to even small amounts of mercury (Hg) can cause serious health problems in people. Therefore, many assessments of mercury exposure levels in various countries have been conducted during recent decades. Mongolia is a mining-rich country that in 2000 earned approximately equal amounts of export revenue from mining and livestock. Increasing large-scale and rampant small-scale mining activity in Mongolia is raising fears about the possibility of regional environmental pollution. River water and atmospheric mercury were collected between 26 August and 7 September 2014. In this region the people who engaged mercury mining was called as Ninja. With the hearing survey, they said mercury is not used in their mining area however, high mercury concentration (1,300 ng/L) in river water was observed. In addition, high mercury concentration in the atmosphere is also observed. Based on our results, we conducted human health risk assessment (Hazard Quotient, Hazard Index) which is provided by the US EPA. Result from the risk analysis, not only the people who worked near the mining activity site but also residents near the mining site may at risk.

TP-100

MERCURY POLLUTION BY GOLD MINING IN CHOCO, COLOMBIA

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Mercury (Hg) is one of the most harmful pollutants. The release of this metal into the environment from gold mining activities represents a risk to human health and the ecosystem. The aim of this study was to assess the levels of total Hg (T-Hg) in human hair and several environmental matrices within the Biogeographic Choco area, at the Colombian Pacific region. Total Hg levels were measured using pyrolysis coupled with atomic absorption spectrometry. The median T-Hg level in human hair samples from Quibdo, Choco´s most populated city, was 1.36 µg/g (range: 0.02-116.4 µg/g), whereas in Paimado, a place near gold mining operations on the Quito River, an affluent of Atrato River, it was 0.67 µg/g (range: 0.07-6.47 µg/g). In Quibdo, air samples within gold shops displayed Hg concentrations two orders of magnitude greater than those found in reference sites. Although extensive gold mining activities are carried out in several affluents of Atrato River, sediment samples from places along the river stream showed relatively low levels of T-Hg, probably because of high flow conditions due to abundant rainfall present all year-round. However, it is clear that Hg released from gold extraction is spread through the ecosystem, as T-Hg levels were found to increase according to the trophic level of examined fish species. In some carnivorous fish, average T-Hg concentrations were above international guidelines, especially in Pseudopimelodus schultzi, Ageneiosus pardalis, Sternopygus aequilabiatus, Rhamdia quelen and Hoplias malabaricus, whereas low T-Hg levels were registered in Cyphocharax magdalenae and Hemiancistrus wilsoni. In short, the use of Hg in gold mining in this region of Colombia is causing its bioaccumulation in wildlife and humans, threatening biodiversity and human health.

TP-101

DISTRIBUTION OF TOTAL AND ORGANIC MERCURY CONCENTRATIONS IN SOILS AROUND ASGM AREA, WEST JAVA, INDONESIA, AND DEPENDENCE OF MERCURY CONCENTRATIONS ON ORGANIC MATTER CONTENT

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The distribution of total mercury (T-Hg) and organic mercury (org-Hg) in the soil around the artisanal and small-scale gold mining (ASGM) area along the Cikaniki River was investigated. The soil samples were collected from two sites in the forest near the ASGM village and four sites in the national park, approximately 13 km upstream from the ASGM village. The samplings were conducted in March and August 2014. At each site, after the fallen leaves and branches were collected, the soil samples were collected every 2 cm from the surface up to a depth of 20 cm. The samples were placed in plastic bags with seals and brought back to laboratory. The samples were freeze-dried, ground with agate mortar, and used for determination of T-Hg and org-Hg concentrations, total organic carbon (TOC) and total nitrogen (TN) contents, and chemical composition of the soil. The T-Hg concentration was measured by cold vapor atomic absorption spectrometry (CVAAS) after nitric, perchloric, and sulfuric acid digestion of the samples. The org-Hg was extracted from solid samples using hydrochloric acid/toluene/L-cysteine and measured through CVAAS after mixed acid digestion in the same manner as that for T-Hg. The average concentrations of T-Hg in the forest soils of national park and those near the ASGM village were 1.1 mg kg1 and 1.4 mg kg-1, respectively. The average concentrations of org-Hg in these areas were 3.2 mg kg1 and 3.0 mg kg1, respectively. The average concentrations of T-Hg in the fallen leaves collected from these areas were 1.1 mg kg1 and 4.9 mg kg1, respectively. The T-Hg concentration in the soil varied with depth tending to show the highest values at the surface or the layers several centimeters from the surface. The org-Hg and TOC contents showed similar vertical variations as that shown by T-Hg, except for the near-surface layers containing TOC greater than 30%. A linear relations were observed among TOC, T-Hg and org-Hg for the samples containing TOC smaller than 30%. From the relation between TOC and TN, it was suggested that the samples having TOC greater than 30% contain insufficiently decomposed fallen leaves. The mercury discharged into atmosphere by mining activities is transported to a remote site and causes an increase in the mercury concentration at the surfaces by deposition. The mercury deposited on the surfaces can be trapped and retained by organic matter and then subjected to methylation with the decomposition of the organic matter.

TP-102

RISK OF MERCURY METHYLATION IN RIVER SEDIMENTS OF GOLD MINING COMMUNITIES IN SOUTHWESTERN GHANA, DUE TO MERCURY AND CYANIDE EXPOSURE

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Mercury and cyanide interaction in the aquatic environment of gold mining communities, increases the solubility of mercury. This causes Hg to be highly bioavailable for methylation. Hence, cyanidation and amalgamation techniques adopted respectively by Large Scale (LSGM), and, Artisanal and Small-Scale (ASGM) gold miners in Southwestern Ghana makes it imperative to investigate the levels of methylmercury in Hg-contaminated aquatic environments loaded with cyanide. Total and Methylmercury levels in sediments from Rivers Aprepre and Ankobra located in the Prestea-Huni Valley district of Southwestern Ghana have been investigated. Total mercury content was determined by CV-AAS after acid digestion with HF/HNO3/HCl. Extraction of MeHg from sediment was achieved using H2SO4/KBr/CuSO4 and methylene chloride. This was followed by aqueous phase propylation coupled to purge and trap -GC-AFS detection. MeHg in sediments from River Aprepre (known to receive effluent from both ASM and LSM) varied between 6.11 to 14.83 ng/g (2.5-3.7% of THg), whilst THg ranged from 241 to 405 ng/g dry mass. MeHg in sediments from River Ankobra (which is further away from cyanide exposure) ranged from 0.09 to 0.24 ng/g (0.08-0.12% of THg), with total mercury (THg) varying from 76 to 307 ng/g dry mass. Further investigation on temperature fractionation and water solubility (Milli-Q water and Rain water) is on-going to identify the various mercury compounds, and the water-soluble Hg compounds respectively to aid the verification of the MeHg levels in the sediments from the two Rivers. Temperature fractionation is being carried out with a Jozef Stefan Institute in-house designed apparatus; which consist of CV-AAS detector (Lumex, RA-915+), Pyrolytic cell, Pyro-915+ pump, tube furnace etc. Results from these experiments would be presented.

TP-103

Rapid Assessment of ASGM and Other Surface Mining Disturbance through Visual Search of Google Earth Imagery: Case Studies of Watersheds in Indonesia, Laos, and Myanmar

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Southeast Asia has experienced a tremendous upsurge in Artisanal and Small-scale Gold Mining (ASGM) and other surface mining in recent decades, leading to concerns over environmental and human health impacts, particularly associated with widespread use of mercury (Hg) in ASGM. Researchers, conservationists and government authorities need ways to quickly identify the magnitude and extent of land/water areas impacted directly or indirectly by ASGM and other surface mining to assess priorities for further investigation, particularly regarding mercury use and its impacts on environmental and human health.

This poster presents results of a rapid assessment of ASGM and other surface mining disturbance in important watersheds in Indonesia, Laos (Lao PDR) and Myanmar where mining has proliferated over the past two decades, conducted through systematic visual search of imagery (available as of May 2017) in Google Earth Pro 7.1.8.3036 (GEP). This approach allows rapid identification of areas impacted by mining, thereby providing an information baseline for planning research, monitoring and conservation.

The rapid assessment approach uses typical visual characteristics of ASGM and other surface mining disturbance (e.g., changes in spectral reflectance of ground surface from primarily green to white, beige or brown associated with removal of canopy vegetation cover and excavation, presence of small- to medium-sized pits filled with water of different colors (e.g., green, turquoise), discoloration of watercourses) as a search image for use in searching imagery. Searching begins with watercourses as top priority and systematically expands to other areas (e.g., plateaus, mountains) that are likely to have mining impacts. Caveats of the approach are that it is not 100% accurate—areas can be missed and misidentified—and does not provide a quantitative estimate of area impacted by mining.

The rapid assessment approach was used to assess ASGM and other surface mining disturbance in: (1) Batang Hari River watershed, Jambi Province, Sumatra, Indonesia; (2) Sekong River watershed, Attapeu and Sekong Provinces, Laos; and (3) Upper Ayeyarwaddy River and Chindwin River watersheds, Myanmar. Results are presented. Each case study also had a unique component. The Myanmar study compared rapid assessment results to results in an existing database. The Sumatra study traced development of mining by analyzing historical imagery in GEP. The Laos study attempted to quantify mining areas in one subwatershed using draw tools in GEP.

2g: Legacy site assessment and management

TP-104

SEDIMENT – WATER EXCHANGE OF TOTAL MERCURY AND MONOMETHYLMERCURY IN A MERCURY CONTAMINATED MANAGED FLOOD CONVEYANCE SYSTEM

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Yolo Bypass is the largest flood bypass in the Sacramento Valley, California. During high flow flood events, water is diverted into the Yolo Bypass from the Sacramento River to control river stage and protect the city of Sacramento from flooding. Climate change projections for the region indicate the risk of flooding will increase. An increase in flooding would result in increased connectivity of the flood plain with downstream habitats as well as provide conditions favorable for the in situ production of methylmercury (MeHg) in an area burdened by mercury contamination resulting from historic mining activities upstream. Conversion of inorganic mercury (Hg) to the more toxic organic form, MeHg, in freshwater systems is generally accepted to be mediated by bacterial activity. There are a number of environmental variables (organic carbon, sulfate, oxygen) and conditions (temperature, porosity, soil type) that could influence the net production of MeHg and its ultimate release into the water column. This study investigated sediment-water exchange of both total Hg and MeHg from different habitat types in the Yolo Bypass including wild rice, white rice, seasonal wetlands, irrigated pasture, non-irrigated pasture, fallow land, farm land, freshwater tidal wetland, and agricultural drain. Fluxes were determined by a direct assessment using incubated cores and measuring change in overlying water concentrations over short time scales (<25 hrs). Fluxes of total Hg and MeHg ranged from -621 to 787 ng m-2 d-1 and -11 to 29 ng m-2 d-1 respectively with negative values indicating flux into sediment. Agricultural, pasture, fallow, and seasonal wetlands were sources of MeHg with fallow and seasonal wetlands having the highest fluxes. In contrast, drainage canals and freshwater tidal wetlands were sinks and had fluxes into the sediment. These results will be used in the Dynamic Mercury Cycling Model (D-MCM) and integrated with hydrodynamics of the Yolo Bypass to improve our understanding of factors controlling production and transport of Hg and MeHg in the Yolo Bypass.

TP-105

PREDICTING RESPONSES IN PHYSICAL AND BIOLOGICAL COMPARTMENTS TO REDUCTIONS IN MERCURY LOADING FROM RIVER BANKS

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Historical mercury (Hg) releases occurred at a textile manufacturing facility on the South River, VA. These releases resulted in increased Hg concentrations in biotic and abiotic media, which have not declined over the past thirty years in some media (e.g., fish tissue), as originally expected. Introduction of legacy Hg impacted soils to the South River through bank erosion is the most significant source of Hg loading to the system. Interim remedial measures targeted at reducing this source within the first few river miles were initiated in 2016.

As part of the remedy selection process, a set of robust statistical models were developed to predict responses in physical and biological media associated with completion of the interim measures (i.e. bank stabilization). The models integrated site-specific data collected over more than a decade and built upon the detailed conceptual model. Model parameters included total mercury (THg) and methylmercury (MeHg) concentrations in a number of physical media (e.g. sediment, soil, and surface water); biological (e.g. fish tissue) as well as meteorological, adjacent land use and stream discharge data. Different remedial scenarios (i.e. 50% and 100% reduction in Hg loading from eroding banks) were evaluated in order to inform remedial decision making. Model runs predicted significant THg reductions in surface water and sediments adjacent to and downstream of the proposed interim measures.

A short-term monitoring (STM) program comprised of multiple lines of evidence is being instituted that aims to document the predicted reduction in Hg concentrations in a range of biotic and abiotic endpoints. The STM program is intended to evaluate changes in Hg concentrations at specific bank segments following remediation over a relatively short time period (i.e. 2-10 years). Key learnings from the Pilot Bank Stabilization project monitoring program on the South River were built into the STM program in order to maximize the ability to not only detect reductions in Hg loading attributable to the interim measures, but also to be able to differentiate those from changes that may be due to other sources.

This presentation will expand upon the conceptual site model, outline the input/output of the statistical model, review baseline STM data and discuss their importance in an adaptive management remedial framework.

TP-106

Mercury Recovery for Hg Waste by Thermal Process

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This study provides a result of mercury recovery characteristics for waste using thermal technology. Mercury waste was categorized as three types such as waste consisting, waste containing, waste contaminated of mercury or mercury compounds. Those mercury wastes should be properly collected separately and recovered mercury or stabilized for environmentally sound management. Thermal treatment was conducted to recover elemental mercury from mercury containing products (barometer and UV lamp) and Hg contaminated soil. 150 L volume stainless steel drum was introduced inside of the pilot-scale furnace for thermal treatment. An agitator was kept operating during thermal treatment if mixing is needed. Experiments were carried out in temperature range between 550-750°C with reduced pressure condition up to 1,013.25 Pa. Off-gas generated form thermal furnace was passed through a ceramic filter unit. That is used to filter out impurities in flue gas with higher temperature than boiling point of mercury in case of necessary cleaning selectively. 100 kg of waste per batch could be treated and elemental mercury was recovered with a condensation unit by maintain the temperature around 10°C during thermal treatment. Activated carbon trap was applied to control mercury in emitting gas. Also mass balance was made to observe mercury distribution in pilot scale process. Treated waste could be disposed as general waste and recovered mercury could be recycled and reused as a resource.

TP-107

STUDIES TO EVALUATE CONTROLS ON MERCURY BIOAVAILABILITY AND USE OF IN-SITU AMENDMENTS IN TIDAL MARSHES OF BERRY'S CREEK, NEW JERSEY

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Berrys Creek (New Jersey, USA) is an urbanized tidal tributary to the Hackensack River which is in many ways characteristic of urbanized tidal creek-marsh systems dominated by Phragmites. The detrital food web of the Berrys Creek Study Area (BCSA) supports mummichogs and white perch, and the bird community includes sandpipers, red-winged blackbirds, and herons. In the mid-2000s, in association with an Remedial Investigation/Feasibility Studyconducted under Superfund, we initiated a series of studies (1) to better understand the factors controlling mercury geochemistry, bioavailability, and bioaccumulation in BCSA marshes, and (2) to evaluate the potential efficacy of using activated carbon (AC) -based amendments in situ to reduce environmental risks from sediment-associated mercury and PCBs in these marshes.

Building on data from related studies, a substantial field pilot study was conducted in Nevertouch Marsh within the BCSA, in order to assess the benefits of applying thin-layer treatments with SediMiteTM, Granular Activated Carbon (GAC), and GAC + sand. The purpose was to evaluate in-situ treatment effects on Hg, MeHg and PCB bioavailability (porewater) and biouptake (amphipods). The study involved pre-treatment sampling, and spring and fall sampling and analysis of all media over 2 years. Additionally, in situ and laboratory bioaccumulations studies were done to assess AC effects on Hg/MeHg and PCB biouptake.

Results from the Nevertouch Marsh Field Pilot Study and associated bioaccumulation tests provide important information for evaluating the efficacy of in situ treatment of BCSA marshes with AC-based amendments. Specifically, compared to controls, in situ treatment with AC-based amendments: (1) Was highly effective for reducing the bioavailability and biouptake of PCBs, (2) Reduced Hg concentrations in porewater and detritus, (3) Reduced Hg biouptake in caged amphipods (Leptocheirus), (4) Reduced MeHg levels in porewater in the 28-day bioassay with Leptocheirus, and (5) Reduced MeHg biouptake in the 28-day bioassay with Leptocheirus (on days 7 and 14). SediMiteTM treatment consistently performed better than GAC and GAC + sand. Combined with data from related studies, results from the Nevertouch Marsh Field Pilot Study are very helpful for informing the BCSAfeasibility studyand improving our understanding of Hg dynamics in tidal marsh ecosystems.

TP-110

MERCURY DISTRIBUTION IN THE HYEONGSAN RIVER AND ITS TRIBUTARIES NEAR AN INDUSTRIAL COMPLEX IN POHANG

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Recently, there was a report on high mercury concentration in bivalves (Corbicula leana) and sediments near the confluence of the Hyeongsan River and Chilseong Stream located in the southeast of the Republic of Korea. Hyeongsan River supplies drinking water to citizens of Pohang City and currently, the pollution of Hyeongsan River is a big issue.

Given that both Chilseong and Gumu Streams run through the Pohang Industrial Complex and ultimately flow to Hyeongsan River, it is imperative to study if there are any impacts of industrial effluents on mercury contamination in the two streams and the Hyeongsan River. Thus, the objective of this preliminary study was to examine total and methyl mercury concentrations in sediments collected from Gumu and Chilseong streams and from Hyeongsan River. Sediments and water were collected from over 30 stations along with Hyeongsan River, Gumu Stream, and Chilseong Stream and analyzed for total mercury (THg) and methylmercury (MeHg) using Cold-Vapor Atomic Fluorescence Spectrometry. Average concentration of THg was highest in Gumu Stream (78.8±84.3 mg/kg dw), followed by in Hyeongsan River (4.39±9.70 mg/kg dw) and Chilseong Stream (0.30±0.42 mg/kg dw). Similarly, average MeHg in Gumu Stream, Hyeongsan River, and Chilseong Stream were 151±237, 3.19±6.77, and 0.67±1.12 μg/kg dw, respectively. Further study will be necessary to investigate major sources of Hg in Gumu Stream and to evaluate the impacts of Hg transport to the adjacent Hyeongsan River.

TP-111

CALIFORNIA STATEWIDE MERCURY CONTROL PROGRAM FOR RESERVOIRS

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Mercury in fish is a widespread problem and source control alone will not solve this problem in most California reservoirs in a reasonable amount of time. Therefore, California's Environmental Protection Agency (Cal/EPA) is developing an innovative statewide mercury control program for reservoirs. This poster provides an update on California's program since ICMGP 2015 (S04).

Fish methylmercury levels are elevated in about half of all California lakes and reservoirs sampled. In addition, the California Office of Environmental Health Hazard Assessment has issued many advisories for limited or no consumption of many popular sport fish in California lakes and reservoirs. The inability to safely consume fish from many California lakes and reservoirs devalues California fisheries as a food source for humans and wildlife.

Mercury impairment is due to several inter-related factors: inorganic mercury sources; conditions in reservoirs that cause the conversion of inorganic mercury to methylmercury and its subsequent bioaccumulation in the food web; fish species present; and in some cases depressed primary and secondary production. Reservoir creation and management may exacerbate the mercury impairment by increasing methylmercury production and bioaccumulation.

The project involves: identifying mercury sources to reservoirs; evaluating reservoir, watershed, and fisheries conditions; determining the linkage between reservoir fish methylmercury levels, reservoir and watershed conditions, and mercury sources; and identifying controllable factors that determine reservoir fish methylmercury levels.

The potential solutions to reduce fish methylmercury concentrations are three-pronged: (1) mercury source reductions, (2) reservoir water chemistry management, and (3) fisheries management. This proposed statewide mercury control program for reservoirs encourages innovation in reservoir water chemistry (e.g., oxidants to hypolimnion) and fisheries management (e.g., intensive fishing; new or changes to fish stocking practices; and nutrient additions to slightly increase chlorophyll-a concentrations in oligotrophic reservoirs).

More information is available on the project website.

TP-112

A FIELD TEST OF IN-SITU AMENDMENTS AS POTENTIAL REMEDIATION TOOLS FOR METHYLMERCURY IN PENOBSCOT RIVER, ME, SALT MARSHES

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Surface applications of black carbons and other treatments were tested as potential tools for methylmercury (MeHg) risk mitigation in a Hg-contaminated tidal salt marsh in the Penobscot River, ME. Four surface amendments were tested, activated carbon, a pine dust biochar, ferrous chloride (FeCl2), and lime. Field studies across the Penobscot system pointed to salt marshes as sites of particularly high methyl Hg production and accumulation, and therefore a key target for remediation. The study design was a fully-crossed small plot study, with five treatments at each of two sites on a large marsh platform at mid-salinity. The sites were chosen to represent two different major habitats in the marsh.

Plots were initially treated in Sept. 2010, and were sampled four times post-amendment, through Sept. 2012. The main study endpoints were pore water MeHg concentrations and sediment water partition coefficients, presumptive indicators of bioavailability to benthic biota. The treatments were generally well-retained in the plots, and it was visually obvious that the carbons penetrated deeper into surface soils over time.

Both activated carbon and biochar amendments were effective in reducing Hg and especially MeHg concentrations in pore waters at both study sites in Mendall Marsh. AC amendments reduced pore water MeHg concentrations at the both sites by >90% at the one month time point and by 60% to 70% on average across all the four time points through two years.

Biochar was only a little less effective than AC. Lime and FeCl2 additions had no significant impacts on either total Hg of MeHg pore water concentrations. In general, the black carbon amendments did not have any significant impact on surficial pore water chemistry.

AC and biochar reduced MeHg risk primarily by increasing MeHg partitioning to the solid phase (i.e. reduction in pore water MeHg concentration), rather than by reducing the bioavailability of inorganic Hg for methylation. The next step in evaluating this tool in the Penobscot would be larger-scale, longer-term plot studies. These studies should include evaluation of long-term changes in MeHg accumulation in soils, as well as studies of animal bioaccumulation, food web structure, plant community structure, marsh productivity and Hg/MeHg flux. Large plot studies would also provide a better estimate of the cost of treatment.

TP-113

PATTERNS OF MERCURY RELEASE FROM PROFUNDAL SEDIMENT OF CALIFORNIA RESERVOIRS UNDER OXIC AND ANOXIC CONDITIONS

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Inorganic Hg, predominantly from widespread atmospheric deposition, but also from point sources including mine and industrial sites, is transformed to methylmercury (MeHg) by anaerobic bacteria in oxygen-poor water and sediment. The profundal zone of productive lakes commonly exhibits summertime anoxia and associated accumulation of MeHg in bottom waters. MeHg in bottom water bioaccumulates in pelagic biota when it diffuses upwards across the thermocline or when MeHg-rich bottom water mixes into the upper water column. With the shortcomings of conventional Hg control strategies, such as dredging, capping, watershed controls and source control, managers are increasingly interested in developing in situ strategies to repress Hg bioaccumulation in managed aquatic ecosystems. One potential

strategy is to enhance the redox potential at the sediment-water interface to repress MeHg efflux to overlying water. In this study we present a conceptual model of MeHg cycling at the profundal sediment-water interface and summarize redox-mediated mechanisms that enhance MeHg efflux, including MeHg production by sulfate-reducing bacteria, release of MeHg from metal hydroxides in sediment, demethylaing capacity of aerobic and anaerobic bacteria, and enhanced MeHg mobility under sulfidic conditions. We then present highlights of experimental sediment-water chamber incubations from a number of California reservoirs. Sediment generally showed enhanced efflux of MeHg under anoxic conditions relative to oxic conditions. Typical anoxic release rates of MeHg ranged from 20-150 ng/m2/d. Some chambers showed a correlation between sulfate uptake and MeHg production, and some chambers showed a distinct drop in MeHg accumulation corresponding with the disappearance of sulfate. One interesting observation common to most experiments was a loss of MeHg from chamber water near the end of the anoxic phase of the incubations, suggesting either a shift in the relative importance of methylation and demethylation and/or a sorption sink, perhaps via iron sulfide formation under sulfidic conditions. At one contaminated study site, oxic conditions, while lowering MeHg efflux, resulted in enhanced efflux of ionic mercury, sulfate and iron, suggesting enhanced oxidative dissolution of sulfide minerals with the co-release of mercury. With a more comprehensive understanding of MeHg cycling at the profundal sediment-water interface, managers will be better able to develop effective management strategies aimed at repressing MeHg bioaccumulations in lakes and reservoirs.

TP-114

HEAVY METALS GOT YOU DOWN? TREATMENT OPTIONS FOR MERCURY AND METHYL MERCURY

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Background/Objectives. Heavy metals such as Mercury (Hg) as well as Methyl Mercury (MeHg) are widely distributed and persistent pollutants in the environment. Although all contaminated sites are unique and a site-specific approach to remediation is often required, heavy metal contamination creates even more complex challenges. Remediation methods in general use include isolation, immobilization, toxicity reduction, physical separation and extraction. The ecological and human health effects of Hg, and MeHg are generally related to the environmental transformations. For example, inorganic mercury can transform to the more toxic monomethylmercury (MeHg) in anaerobic environments such as contaminated sediments. Biomagnification of MeHg in the aquatic food web and consumption of fish and shellfish contaminated with MeHg is the primary route of human exposure to Hg(II). MeHg is toxic to both humans and fish. Almost all mercury in fish is MeHg. MeHg is formed largely in anoxic sediments from inorganic mercury methylation mediated primarily by sulfate reducing bacteria. The bottom sediments are the main reservoirs of mercury and to the extent that this mercury is available to overlying water is a sensitive indicator of risk to the aquatic ecosystem. Effective remediation of such sediments to reduce the release of mercury is essential to minimize the contamination of fish and shellfish with MeHg. Experimental results will be presented that demonstrate the efficacy of Mn-based adsorbents for immobilization of Hg (II) and demethylation of MeHg to Hg(II).

Results. A laboratory investigation was conducted to assess the feasibility of immobilizing Hg and demethylating MeHg using iron (Fe) and manganese (Mn) mixed metal oxides. Batch sorption screening test results indicate >99% removal of Hg from aqueous batch reactors. Anaerobic batch microcosms were conducted with Hg-spiked sediments amended with Mn-based oxides to evaluate demethylation as a result of manipulating the redox conditions from reducing to oxidizing. The results of these batch studies will be presented as well as preliminary results from a pilot-scale test.

TP-115

INVESTIGATING THE ROLES OF COMPETING SULFIDE AND ORGANIC LIGANDS IN ULTRAVIOLET ACTIVATED MERCURY REMOVAL FROM WASTEWATER

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This work presents findings on the developments of a photochemical treatment method for Hg removal from organic-rich secondary process chlor-alkali wastewater (i.e., conventionally treated with sulfide) that resulted in removal of dissolved ppb Hg down to low ppt Hg levels (<<40.0 ppt Hg). The method, termed ultraviolet activated chelation (UVAC), uses high intensity ultraviolet irradiation at 254 nm (UV-C) followed by sub-micron filtration (0.45 m). Hg removal results are presented as unfiltered and filtered Hg effluent following UVAC treatment with variable pH and UV-C irradiation periods. Low-level ppt Hg results in filtered effluent are shown to occur by chlor-alkali UVAC photo-chemical processes in both Hg wastewater and Hg solutions of DI water and variable IHSS dissolved organic matter and sodium sulfide prepared under open atmosphere. The findings lead to a discussion of theoretical explanations for the observed filterable Hg formation, including the importance of sulfide and photo-activated organic binding ligand action in photochemical valence transfer within soluble Hg complexes. Possible future work follows to include experimental measurements that could further develop UVAC as a viable Hg removal technology for wastewater with variable halide and organic chemistry.

TP-116

IMPACT OF HISTORIC LEAD ZINC MINING ON MERCURY ACCUMULATION IN FISH IN COOKS POND, NEW HAMPSHIRE, USA

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High Hg concentrations in New Hampshire fish have been attributed to atmospheric deposition associated with global anthropogenic emissions initiated during the industrial revolution. However, significant local sources of Hg may exist from mine tailings associated with abandoned lead-zinc mines in eastern New Hampshire and western Maine. The Madison Lead Mine in New Hampshire, most active in the early 20th century, produced a tailings fan (0.7 ha) that extends into Cooks Pond (14.3ha). Pond sediments have concentrations of Pb (>6,400ppm) Zn (>11,200ppm) and Hg (>450ppb) that are significantly higher than sediments from surrounding lakes. Mercury in the mine tailings is likely derived from a variety of brown sphalerite that is found within the ore body that contains up to 11,000ppb Hg.

Eight sediment cores (90mm diameter) were collected from Cooks Pond together with cores from downstream Silver Lake and nearby (2km) Durgin Pond using a Uwitec gravity corer. Cores were collected in water depths ranging from 4.5m to 7.5m and were 60-100cm in length. Fish (pickerel, yellow perch, sunfish) were collected by seine net and hand line. Cores were scanned using an ITRAX core scanner and were subsampled at 3-50mm intervals. All samples of fish and sediment were analyzed for total Hg using a Teledyne Leeman Labs Hydra C mercury analyzer.

The concentration of Hg in sediment cores from Cooks Pond, co-varies with Pb and Zn, with the highest concentration (460ppb Hg) occurring approximately 7cm below the sediment water interface. Concentrations in the sediment also increase with proximity to the onshore tailings deposit. If Hg was only derived from atmospheric deposition, its concentration would be expected to decrease with proximity towards the source of the tailings due to sediment dilution. In nearby Durgin Pond, the highest Hg concentration (320ppb) occurs just 1cm below the sediment water interface reflecting Hg derived primarily from atmospheric deposition.

Higher Hg concentrations would be expected in fish from Cooks Pond given the higher concentrations in the sediment, however it was found that Durgin Pond fish of similar length, weight, and species had consistently higher Hg concentrations (350ppb vs 90ppb). This is likely due to two factors. First, much of the mine tailings Hg is mineral bound and not bioavailable, and second, there are more wetlands surrounding Durgin Pond allowing for more Hg methylation. Therefore we conclude that despite adding Hg to the ecosystem, mining has not led to higher concentrations of Hg in fish.

TP-117

A MECHANISTIC MODEL FOR INORGANIC AND METHYLMERCURY TRANSPORT AND CYCLING IN THE YOLO BYPASS, CALIFORNIA - A MERCURY CONTAMINATED FLOODPLAIN

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The California Bay-Delta region is impacted by mercury contamination from historical mercury and gold mining upstream. Microbial activity in downstream aquatic environments can convert inorganic mercury into methylmercury (MeHg), a toxic and readily bioaccumulated form of mercury. The Delta Mercury Control Program (DMCP) was established in 2011 to protect human and wildlife health from MeHg exposure. It requires the California Department of Water Resources to conduct control studies to evaluate whether operational changes or other practices could be implemented to reduce ambient MeHg loads to Delta open waters and the Yolo Bypass, a floodplain area inundated by managed flows. A mechanistic model of mercury cycling is being applied in the Yolo Bypass as part of a multi-agency modeling, field data collection, and experimental program to identify options to reduce MeHg supply and meet DMCP regulatory requirements. The Dynamic Mercury Cycling Model (D-MCM) is a time-dependent 1D-3D mechanistic aquatic mercury cycling model that includes inorganic Hg(II), methylmercury and elemental mercury in water, sediments and a food web. Hydrodynamic inputs for D-MCM are generated with TUFLOW, a high resolution hydrodynamic model. A coarser 47 cell grid for mercury simulations was developed based on 5 criteria: land use, disked/non-disked land, THg concentration in sediments, percent time wet, and wet/dry cycling frequency. Model simulations span 1997-2012. D-MCM is currently being used to predict concentrations and mass balances of inorganic and methylmercury in the Yolo bypass, considering various influences on methylmercury production and concentration, including hydrology, particle dynamics, vegetation, and inorganic mercury contamination. Predicted exports of inorganic Hg and MeHg from the Yolo Bypass are being used as inputs to a companion mercury modeling effort for the downstream Sacramento San Joaquin RIver Delta system.

TP-118

EVALUATION OF INORGANIC AND CARBON-BASED MATERIALS FOR MERCURY STABILIZATION WHEN CO-BLENDED WITH CONTAMINATED RIVER SEDIMENT: A COLUMN STUDY

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Mercury (Hg) sequestered in soils and sediments in riverine systems can be mobilized as a result of flooding and precipitation events, acting as a secondary source of contamination to the river. Remediation of this Hg is often complex, greatly depending on the scale of Hg distribution and the influence of Hg transport and deposition processes. At some contaminated sites, partitioning of Hg to reactive amendments may be implemented to stabilize Hg in situ, rendering it relatively immobile and less bioavailable. Saturated column experiments were conducted to evaluate the effect of several inorganic and carbon-based amendment materials on Hg immobilization and transport. Columns were filled with Hg-contaminated sediment collected from the South River, VA, amended with a selected reactive material, and were continuously flushed with low-Hg river water from the South River for more than 6 months. The inorganic amendment columns included sediment blended with a 2% dosage (dry weight) of limestone, unmodified clay or sulfidized clay. The carbon-based amendment columns consisted of a 2% (dry weight) dosage of unmodified biochar, HNO3-modified biochar, sulfidized biochar or a 5% dosage of sulfidized biochar. A control experiment including a column packed with unamended sediment was run to establish baseline Hg concentrations and geochemical conditions. The results of the experiments indicate that the addition of limestone, unmodified biochar and HNO3-modified biochar to contaminated sediment had little effect on Hg transport under saturated conditions. Leaching of both filter-passing (<0.45 mm) and particulate Hg from these amended systems was similar in magnitude to the sediment control. In contrast, extensive Hg mobilization was observed in the sediment amended with unmodified clay. Cumulative filter-passing Hg measured in the effluent of the clay-amended sediment increased by more than 200% when compared to the control, suggesting destabilization of Hg previously sequestered in sediment and colloid-facilitated transport in the presence of the clay amendment. Mercury transport was greatly reduced when sediment was blended with either sulfidized clay or sulfidized biochar. The cumulative release of filtered Hg measured in the effluent of both the sulfidized clay-amended sediment and the sulfidized biochar-amended sediment (2% dosage) was 24% of the control and 29% of the control, respectively. A further reduction of Hg leaching was observed when the amendment dosage of sulfidized biochar increased from 2% to 5%. The strong interactions between Hg and S may have resulted in increased binding of Hg to the S-modified materials, effectively sequestering Hg within the sediment.

TP-119

MERCURY PARTITIONING TO CLAY SIZE FRACTIONS FROM A CONTAMINATED FLOODPLAIN SOIL

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Clay particles (< 0.002 mm) can dominate trace element sorption in soils because of their large surface area per unit mass. However, the smaller clay size fractions are also potentially mobile allowing for leaching and loss of particulate Hg from the soil profile. To investigate the extent to which clay particles dominate Hg sorption we size fractionated eight soil samples collected from a contaminated floodplain soil that had been impacted by a chlor-alkali facility. The study site is located in Berlin, New Hampshire; multiple soil cores were collected on the floodplain at increasing distance from the original Chlor-alkali facility; selected samples from different cores and of varying total Hg content and depth in the profile were used for size fractionation. Initially the soil sample (ca. 10g) was dispersed in 50 ml of deionized water by sonication. Four clay fractions were then separated by gravitational settling (2-1 μm) or centrifugation (1-0.5 μm), 0.5-0.1 μm, 0.1-0.05 μm. The final supernatant was retained to study the dissolved partitioning of Hg by size exclusion chromatography-ICP-MS. The separated fractions were dried and total Hg was determined by acid digestion and ICP-MS analysis. With the exception of one soil sample (23% clay) the other soils were low in clay content (1-4%). The soil samples ranged from 0.07 – 8.2 mg/kg total Hg and, as expected, Hg concentration was increased in the clay fractions compared to the bulk and increased with decreasing particle with the smallest fraction having up to 18 times the corresponding bulk soil Hg concentration. Excluding the high clay soil sample, the clay fractions made up, on average, 2% of the total soil mass but contained 17% of the total Hg. The two larger clay fractions, despite being lower in Hg concentration, contained the majority of Hg because they constituted most of the clay mass. Size exclusion chromatography-ICP-MS revealed that Hg in the aqueous phase after the final clay separation was bound in nanoparticle complexes. The average percent of the total soil Hg in the < 0.5 μm was 8% and indicated that particulate transport of Hg from these soils was likely an important process.

TP-120

LABORATORY METHODS FOR ASSESSING THE EFFECTS OF ACTIVATED CARBON-BASED AMENDMENTS ON THE BIOAVAILABILITY OF MERCURY AND METHYL MERCURY TO AQUATIC INVERTEBRATES

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The Berrys Creek Study Area (BCSA) is a tidal tributary of the Hackensack River with a long history of human impacts. The BCSA encompasses the 6.5-mile-long Berrys Creek, its tributaries, and approximately 1,100 acres of tidal wetlands dominated by the marsh reed Phragmites. The BCSA is the subject of an ongoing remedial investigation focused on mercury (Hg) and polychlorinated biphenyls (PCBs) as primary contaminants of interest, their potential for bioaccumulation, and remedial options for reducing their potential bioaccumulation. This presentation focuses on the development of laboratory test methods used to examine the bioaccumulation of Hg in benthic invertebrate test organisms and the effects of activated carbon-based amendments on reducing Hg biouptake.

Preliminary studies were conducted to optimize methods to assess the bioavailability of Hg and methyl mercury (MeHg) in BCSA marsh sediments. Several challenges needed to be overcome in order to successfully conduct the bioaccumulation tests. For example, because the test organisms could not be tested with unprocessed marsh sediment samples, which are made up of sediment mixed into a dense matt of Phragmites roots, the field samples were homogenized before the test. This facilitated survival of the test organisms and reduced the time required to process samples and retrieve sufficient biomass of test organisms for chemical analysis. However, collection and processing of sediment is known to disrupt the geochemical conditions in natural sediment, increase available organic matter and microbial activity, and disrupt the balance of methylmercury production and degradation. Therefore, preliminary studies measured the concentrations of MeHg in sediment and porewater, along with other parameters (e.g., redox, sulfides) over time, to demonstrate that redox and net methylation conditions were reestablished before initiating the bioaccumulation phase of the test. We also tested several approaches to mixing and dilution of field samples.

Subsequent 28-day bioaccumulation tests were conducted to determine if treatment of BCSA sediment with activated carbon (AC) reduces the bioavailability and biouptake of total Hg and MeHg by the amphipod Leptocheirus plumulosus. Concentrations of MeHg in porewater were significantly reduced in AC-treated sediments in comparison to untreated sediments at most time points analyzed. Bioaccumulation of MeHg was significantly reduced in test organisms exposed to BCSA sediment treated with activated carbon-based amendments after 7 to 14 days exposure.

TP-122

LONG-TERM EFFECTS OF MERCURY TOWARDS FRESHWATER BIOFILMS

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Biofilms are well known to be involved in the fate of Hg in lotic systems, by their accumulation, transformations and involvement in its trophic transfer. In contrast, only few are known about Hg impacts on biofilms. The present study aimed thus to examine long-term effects of Hg towards biofilms. To that end, biofilms were grown on microscope glass slides using microcosms filled with Geneva Lake water. Three microcosms were spiked with inorganic IHg at concentrations of 13 ± 2 pM, 131 ± 16 pM and 1.48 ± 0.08 nM (precisely measured), whereas one microcosm was not contaminated and used as a control. After 7 weeks of colonization, biofilms were analyzed for their total THg and intracellular, Hgint, (determined after a washing step with cysteine) IHg and CH_3Hg content. Their compositions were examined based on their ash free dry mass, chlorophyll a content, percentage of abiotic and biotic fractions and taxonomic composition. Grown biofilms were further exposed to 2 nM IHg for 24 h and analyzed for their modification of microorganism cell membrane permeability and oxidative stress.

Biofilms grown in control microcosms were found to contain 0.33 ± 0.01 nmol THg/gdw and 0.13 nmol Hgint/gdw. Exposure to 131 ± 6 pM IHg increased by about 2- and 4- fold THg and Hgint content, respectively. At the highest studied Hg concentration, THg content reached 18.7 ± 6.1 nmol/gdw and Hgint content, 1.9 ± 0.3 nmol/gdw, representing only 10% of the total Hg content. That increase in accumulation was accompanied with a 1.5-fold decrease of chlorophyll a content in biofilms grown in 1.48 ± 0.08 nM IHg. Taxonomic analysis also revealed a shift in algal and bacterial species upon exposure to Hg. The modification of membrane permeability was found to be less important in biofilms grown in IHg than in biofilms grown in the control microcosm. In contrast, pre-exposure to IHg did not prevent biofilms to exhibit oxidative stress. Long-term Hg exposure induced an accumulation of IHg in biofilms as well as a change in microbial communities. Biofilms might thus represent useful bioindicators of Hg effects in natural waters.

TP-123

IMPACT OF RESERVOIR WATER LEVEL MANAGEMENT ON SEDIMENT PORE WATER CHEMISTRY AND METHYLMERCURY PRODUCTION

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Reservoirs typically have elevated fish mercury (Hg) levels compared to natural lakes and rivers. A unique feature of reservoirs is water-level management which can results in sediment exposure to the air. The objective of this study is to identify how reservoir water-level fluctuations impact Hg cycling, particularly the formation of the more toxic and bioaccumulative methylmercury (MeHg). Total-Hg (THg), MeHg, stable isotope methylation rates and several ancillary parameters were measured in reservoir sediments (including some in porewater and overlying water) that are seasonally and permanently inundated. The results showed that sediment and porewater MeHg concentrations were over 3-times higher in areas experiencing water-level fluctuations compared to permanently inundated sediments. Sulfate cycling which is often associated with MeHg production was enhanced in the seasonally inundated sediments; however, statistical analysis showed that the main factors correlated with porewater MeHg concentrations were porewater THg, porewater DOC, and sediment-porewater THg partition coefficients (log Kd). The THg log Kd values showed distinct relationships with sediment organic carbon depending on whether the sediments were permanently are seasonally inundated. Overall, our results suggest that sediment exposure to the air increases organic matter breakdown which promotes the partitioning of THg and carbon into the porewater phase where it enhanced methylation.

TP-126

THE EFFECT OF SOLID PHASE SORBENT MATERIALS ON THE LEACHABILITY OF MERCURY FROM CONTAMINATED SOILS

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Streambank soils within the East Fork Poplar Creek (EFPC) watershed have elevated concentrations of mercury (Hg) as a result of historic use and discharge of Hg into the system associated with activities at the Y-12 National Security Complex. Mercury can leach from these soils as a result of water level fluctuations and erosion of stream banks resulting in the soils acting as a source of Hg to the creek. Laboratory experiments were conducted to examine the amount of Hg leaching from two soil samples collected from EFPC and a soil sample collected from Hinds Creek, an uncontaminated creek used as a reference site. For these batch laboratory studies the amount of mercury leaching from the soils when exposed to artificial creek water or water from EFPC was examined for two weeks with samples collected every 3-4 days. After two weeks, solid phase sorbents were added to some of the samples and the amount of Hg leaching from the soils with and without sorbent addition was examined for an additional two weeks. The concentration of Hg in the reference soil was 0.028 g/g and the two soils from EFPC had Hg concentrations 100 and 10,000 times greater than the reference soil. After the two week leaching period with artificial creek water, the concentration of Hg in the aqueous solution was 1.6 ng/L in the soils from the reference site and approximately 100 and 4000 times greater in the aqueous phase of the contaminated soil treatments. The solid phase sorbents that were tested included Thiol-SAMMS(r), OrganoclayTM PM-199, OrganoclayTM MRM, SediMiteTM and a biochar. A reduction in the amount of Hg leaching from the soils was only observed when SediMite was added The Hg partitioning coefficients for the three soil samples were similar (log Kd= 4.3-4.7) and these Kd values were greater than the Kds measured with the sorbents and a Hg-DOM solution (no soil present). The results from this laboratory study will help evaluate the usefulness of solid phase sorbent materials as a remedial option for reducing the amount of Hg leaching from soils into EFPC.

TP-128

EVALUATION OF SORBENT MATERIALS FOR MERCURY REMEDIATION IN A FRESHWATER ECOSYSTEM

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Elevated concentrations of mercury are found in stream bank soils and sediments in the East Fork Poplar Creek watershed in east Tennessee, where erosion of stream banks and leaching of mercury contributes to mercury flux into the downstream environment. The use of sorbent technologies is being investigated as a soil or sediment remediation approach to minimize mercury flux and/or mercury available for microbial methylation by sequestering mercury within a high affinity sorbent matrix. The majority of sorbent studies target ex situ removal of inorganic mercury from industrial waste streams. However, for the in situ treatment of a contaminated aquatic ecosystem, sorbents need to be evaluated in the presence of competing ligands, such as natural organic matter (NOM), mineral surfaces, and other constituents present in soils or sediments. These competing ligands can limit the effectiveness of sorbents deployed in situ. We conducted a series of equilibrium sorption batch experiments to evaluate the impact of NOM complexation on sorbent performance. Sorption isotherms were developed both with and without a standardized NOM reference material (Suwannee River NOM) for the following sorbents: Thiol-SAMMS(r), OrganoclayTM PM-199, OrganoclayTM MRM, SediMiteTM, pine wood biochar, lignin-based carbon materials, brass and bone apatite. The presence of NOM significantly decreased the sorption efficiency of inorganic mercury to the sorbents, quantified by the partition coefficients, which were highest for Thiol-SAMMS(r) followed by carbon-based sorbents. The release of solutes from sorbents was also evaluated (e.g., SO42-, NO3-, Cl-), as the leaching of sulfate can result in changes to the pore water chemistry and may enhance methylation of mercury by anaerobic microorganisms. Additionally, the successful use of a sorbent technology hinges on the assumption that mercury bound to a sorbent is no longer available for microbial methylation. To test this assumption, mercury bioavailability was investigated via a series of bioassays employing a pure culture of D. desulfuricans ND132 as a model organism for mercury methylation. The extent and rates of mercury methylation were evaluated in the presence and absence of sorbent materials loaded with inorganic mercury. The results collected to date suggest in situ treatment using sorbents may be a viable option for reducing mercury flux from distributed point-source locations in the EFPC watershed.

TP-129

CHARACTERIZATION OF MANGANESE OXIDE AMENDMENTS FOR IN SITU REMEDIATION OF MERCURY-CONTAMINATED SEDIMENTS

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A new method was investigated for treatment of Hg-contaminated sediments by addition of either pyrolusite (Mn4+O2) or potassium birnessite (K end member of (K, Na, Ca)x (Mn4+, Mn3+)2O4.1.5H2O). The addition of Mn-oxide to Hg-contaminated sediment is hypothesized to buffer redox potential at a level higher than is favorable for Hg methylation. Long-term, sediment tank mesocosm experiments investigated changes in Mn-oxide mineralogy over time and its control on system reduction-oxidation potential. Manganese oxide amendments were either granular pyrolusite (80% MnO2, commercially available) or synthetic powdered birnessite (from KMnO4). Mesocosms consisted of Mn-oxide amendment mixed into the upper 5 cm of wet sediment or applied as a thin-layer sand cap with overlying natural water. Amended sediments were sampled between 4 and 16 months of mesocosm operation, and characterized by X-ray absorption spectroscopy (XAS), powder X-ray diffraction (XRD), and scanning electron microscopy (SEM) to examine changes in Mn solid phases and Mn oxidation state. Manganese in unreacted sediment (bulk concentration 1.3 wt. %) was a mixture of mostly Mn2+-carbonate and sorbed or aqueous Mn2+. Characterization of unreacted birnessite amendment by SEM and XRD indicated poorly crystalline material and particle sizes of a few micrometers. Reducing conditions in the sediment microcosms resulted in transformation of Mn4+-oxides with time. For birnessite-amended sediments, a hydrated Mn3+ oxyhydroxide phase was present after 4 months. With further reaction, Mn was transformed to a combination of Mn2+ carbonate (rhodocrosite) and aqueous or sorbed Mn2+. For pyrolusite-amended sediments, the original Mn4+-oxide was first altered to a mixture of Mn3+ oxyhydroxide and oxide phases with minor Mn2+ carbonate, followed by the transient formation of mixed (Mn3+, Mn2+) oxides, and a progressive increase in the Mn2+carbonate fraction with time. After 16 months of reaction, Mn in solid phases was dominantly Mn2+ carbonate. Slow conversion of Mn4+ oxide to Mn3+ hydrated oxides or mixed-valence (Mn3+, Mn2+)-oxides creates a long-term system redox buffer that makes microbial sulfate reduction less energetically favorable and inhibits methylation of inorganic mercury to methylmercury. Longevity of the amendment treatment to sediments could be controlled to some extent by adjustment of the mass and type of Mn4+ oxide applied, degree of mineral crystallinity, and particle size.

TP-131

HARDWOOD BIOCHAR AS TREATMENT MEDIA IN REACTIVE LAYERS FOR PORE WATER MERCURY IN SATURATED FLOODPLAIN SOILS

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Mercury (Hg) contamination in riverine systems is often widespread in sediments and floodplain soils due to erosion, transport and deposition processes, creating a challenge for remediation. When methylated, Hg becomes much more toxic and can bioaccumulate easily. The primarily biotic process of methylation is often independent of the total Hg concentration, requiring a robust treatment method that can decrease both total Hg and methyl Hg (MeHg). Aqueous Hg leached from contaminated soils and sediments can be present in different oxidation states (e.g., Hg(0), Hg(II)), bound to many sulfur-containing ligands, and complexed with dissolved organic carbon and chloride. The capability of a reactive material to broadly treat these many forms of Hg is key. A series of saturated flow-through column experiments was conducted that evaluated hardwood biochar for removal of Hg derived from a contaminated floodplain soil. These column experiments tested the effectiveness of the biochar with different layer thicknesses and placement geometries relative to contaminated soil, and tracked the impact of the biochar material on MeHg concentrations. Mercury concentrations were tracked both temporally in the effluent and spatially along the column length to determine Hg removal efficiency. Solid samples of the biochar material were collected during and after the experiment from select columns and examined using synchrotron-based confocal micro x-ray fluorescence (CXMFI) spectroscopy techniques. Both the total aqueous Hg and MeHg concentrations declined across the biochar treatment layer in all column experiments. In the column experiments where the biochar was placed immediately adjacent to the contaminated soil, Hg concentrations were observed to increase in the soil pore water, though still declined after passing through the biochar layer, suggesting an interaction between the biochar material and the Hg in the contaminated soil. The results of the CXMFI analysis suggest an increase in Hg loading onto the biochar particles over the course of the column experiments, with Hg observed to be distributed evenly over the particles and adjacent to pore spaces. Overall, the results of the column experiments suggest that hardwood biochar is effective when placed as a treatment layer over contaminated sediment under saturated dynamic flow conditions.

TP-132

A HISTORICAL REVIEW OF REMEDIAL ACTIONS AND RESEARCH CONDUCTED TO MITIGATE MERCURY BIOACCUMULATION RISKS IN OAK RIDGE, TENNESSEE

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Industrial uses of mercury in the 1950s and 1960s resulted in contamination of multiple watersheds in Oak Ridge, Tennessee. Methylmercury concentrations in fish exceed human and ecological risk benchmarks, necessitating implementation of a number of remedial and abatement approaches over the years to try to address the mercury issue. Early actions in the mid-1980s focused on pollution control that positively affected mercury discharges to one local stream, and included consolidation and elimination of untreated discharges, sanitary sewer relining, the construction of a point-source pollution control facility, and replacement of a contaminated settling basin. The 1990s were an intensive period of facility remedial actions designed to improve stream water quality and mercury release. Actions included dechlorinating cooling water discharges, an additional phase of storm sewer relining, the addition of uncontaminated flow from a nearby reservoir, the addition of two small-scale mercury treatment systems, the bypass of stream flow around the replacement settling basin, and the removal of high mercury-contaminated floodplain soils. As a result of almost two decades of facility actions, water concentrations in the receiving stream near the facility decreased steadily from a high of approximately 1700 ng/L to a low of 400 ng/L in 2000, and fish concentrations declined commensurately from a high around 2 mg/kg to a low of 0.6 mg/kg. The positive responses to these actions led to a continued remedial focus on point-source treatment, with two additional facilities going on line (at two separate facilities and watersheds) in the 2000s. Although these facilities have been successful in decreasing water concentrations in the creeks, research suggested that fish concentrations would not decline until water concentrations were below the Tennessee ambient water quality criterion of 51 ng/L. Further, mercury concentrations in fish farther downstream of one facility did not respond to water concentration decreases, and at some sites fish concentrations even increased over historical levels. Although the remedial strategy in Oak Ridge will continue to focus in the near-term on upstream source reduction, recent research suggests that a better understanding of mercury transport, methylation, and bioaccumulation processes in the downstream environment is essential to reduce fish mercury. Since 2014, mercury remediation research and technology development activities have been underway to develop potential remedial solutions for the downstream environment. The Oak Ridge mercury story is a valuable case study for fluvial systems that can inform our national-level understanding of potential mercury cleanup actions and their likely environmental response.

TP-133

THE FORMATION AND SIZE DISTRIBUTION OF MERCURY-BEARING AGGREGATES FROM A CONTAMINATED DIFFUSE SOURCE ZONES SOIL

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Remediation of diffuse mercury source zones poses a unique challenge at a wide range of the 3000 mercury-contaminated sites globally. The existence of diffuse sources is particularly challenging in remediating a low-order stream system (i.e., East Fork Poplar Creek [EFPC]) located in Oak Ridge, Tennessee. The EFPC ecosystem received large point-source discharges during the 1950 and 1960s. Although upstream mercury discharges to EFPC have declined, mercury release persists from point and diffuse sources within the industrial facility where mercury was used and from diffuse downstream sources, such as contaminated bank soils. Previous studies identified the presence of mercury sulfide (HgS) in EFPC bank soils, but the processes that govern HgS formation remain unclear. In this presentation, we report the results from high-resolution electron microscopy and secondary ion mass spectrometry measurements to systematically describe the processes that may lead to the formation of HgS enriched particles in soils. Soil samples were collected from EFPC stream banks and analyzed to identify mercury-enriched particles and to determine their size, elemental composition, and sulfur isotopic ratio. Results from the energy-dispersive X-ray spectroscopy data, confirmed that mercury is generally collocated with sulfur in mercury-enriched particles in EFPC bank soils. Further analysis of the microscopy images indicates that smaller HgS particles hundreds of nanometers in size, aggregate to form the larger micron-sized HgS clusters of 0.15 µm to 4.2 µm in diameter with an average size of 1.4 ± 1.1 µm. We suggest that, these nanometer-sized HgS particles are formed as a result of the precipitation of mercury with microbially produced sulfide. Nanoparticulate or colloidal HgS is widely recognized as a potential source of bioavailable mercury for methylating bacteria. Understanding the mobility and bioavailability of these nanometer-scale particles is an important step in predicting MeHg production in ecosystems.

TP-134

IMPACT ANALYSIS OF MODEL PARAMETER UNCERTAINTY ON MERCURY EMISSION FROM MERCURY DISPOSAL LANDFILL SITE AND METHYLMERCURY EXPOSURES TO HUMAN BODIES

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According to the acceptance of the Minamata convention on

mercury in 2013, final disposal of unused mercury will be requested in the near future. Engineered landfill sites will be one of feasible options for final disposal where dry permanent storage in deep and impermeable underground is geologically impossible. Environmental impact assessment of mercury disposal in engineered landfill sites is necessary to gain public acceptance of mercury final disposal. Numerical simulation using mercury environmental fate models is useful to estimate mercury emissions from landfill sites and its risk. Because the model must include many physical, chemical, and biological reactions like diffusion, adsorption, methylation, and bioaccumulation, it will use many parameters. These parameters strongly depend on the local environment and their values have been reported in the ranges of several orders of magnitude.

The purpose of this study is to assess the impact of model parameter uncertainty on mercury emission from a landfill site and methylmercury exposures to human bodies via polluted fish. A landfill simulation model including mercury reactions was used to assess the impact of model parameter uncertainty on mercury emission from a landfill site. This model includes rainfall penetration into a landfill site, unsaturated water percolation, mercury diffusion, mercury transfer, adsorption, desorption, methylation, demethylation, chemical reduction to elemental mercury, gaseous elemental mercury diffusion in a landfill site, mercury emissions via landfill leachate and gaseous mercury emission from landfill surface. Methylmercury exposures were evaluated using a closed-lake simulation model. This model assumes constant mercury input from the outside and considers mercury reactions including methylmercury biomagnificaiton via food-chain. Precipitation conditions mainly controlled mercury emission. When possible variations of annual precipitation based on 135-year weather records in Japan were considered, mercury emissions at 100-year later since disposal completion was simulated to range from 1.2 to 31 mg-Hg/m2/yr. On the other hand, methlymercury exposures varied much more greatly owing to large uncertainty of model parameters like biomagnification factor. When log-normal distribution were assumed for major model parameters, methlymercury exposures at 10000 years later ranged from 0.122 to 38896 μg-Hg/week/person (65 kg body weight). These results suggest that mercury emissions and exposures to human body, simulated using mercury environmental fate models, inevitably include large uncertainty owing to model parameter uncertainty. Environmental risk of mercury final disposal in a landfill site must be assessed with considering large and unavoidable uncertainty of model simulation results.

TP-135

HARDWOOD BIOCHAR AS A REACTIVE MAT TO STABILIZE MERCURY UNDER ENVIRONMENTAL FLOODING AND DRAINAGE CONDITIONS

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Mercury (Hg) contamination of watersheds due to the release of mercury compounds from industrial activities is a world-wide concern. Mercury compounds once released to the environment can contaminate aquatic systems and provide a long-term non-point source of contamination to downstream and surrounding environments. Mercury stabilization in fluvial settings is challenging due to frequent changes in environmental conditions, including geo-chemical conditions such as redox potential, and physical conditions associated with groundwater discharge/recharge, precipitation, and flooding. A robust remediation system that can stabilize Hg under flooding and drainage conditions without producing unintended consequences is critical to ensure long-term management of contaminated sites in fluvial settings. In this study, hardwood biochar prepared from oak wood was evaluated as a potential reactive media for use in passive reactive mats to stabilize Hg from contaminated river bank sediment and floodplain soil collected near the South River, VA. The purpose of this study is to evaluate the effectiveness of the hardwood biochar on Hg transport and net methylmercury (MeHg) production as a passive reactive mat under environmentally relevant flooding and drainage conditions. Two sets of columns were packed with 50 % v/v of hardwood biochar and quartz sand in an experiment designed to simulate periodic flooding and drainage conditions. The cycling experiment started with dry air and water saturated air, followed by the addition of influent solutions collected from the leachates from contaminated sediment and floodplain soil. After 100 weekly cycles, more than 80% of the Hg present in the sediment and floodplain soil leachates were retained on the biochar, with limited formation of MeHg in both aqueous effluent and the solid materials. The Hg retained on the biochar is likely to present within the porous structure in a form of Hg-S as indicated by micro X-ray absorption spectroscopy (-XAS) and micro X-ray fluorescence (-XRF) maps. A disappearance of sulfoxide functional groups, indicated by sulfur K-edge X-ray near edge absorption spectroscopy (XANES), was observed for the biochar collected from the treatment columns at termination of the experiment. The synchrotron-related analyses suggest that the removal of Hg may involve both filtration by the porous structure and complexation with functionalities or ligands on the biochar. The study results suggest that hardwood biochar may be an effective media for stabilizing Hg under cyclic flooding and drainage conditions without promoting an increase in Hg methylation in both aqueous and solid phases.

TP-136

MERCURY SPECIATION IN A RADIOACTIVE LIQUID WASTE SYSTEM AND IMPACTS ON THE DISPOSAL OF WASTE FORMS

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An estimated 60,000 kg of mercury was discharged into the liquid waste system at the Savannah River Site located near Aiken, South Carolina USA. The mercury is isolated within process vessels and storage tanks, with minimal releases to the surrounding environment. Inorganic mercury was used as a catalyst to aid in the dissolution of aluminum fuel and target assemblies associated with separation processes that supported the US nuclear stockpile. The typical concentration of total mercury in the system is on the order of 100 mg/L. These levels are approximately six orders of magnitude higher than the concentrations that have been studied in most environmental systems.

Liquid waste is a concentrated sodium nitrate solution containing numerous radioactive and non-radioactive elements and ions along with residual inorganic and organic process constituents. The system currently stores approximately 37 million gallons of waste containing approximately 287 million curies of radioactivity. Phases present include an alkaline, high ionic strength liquid phase that is maintained at a high pH (salt solution), a solid phase containing precipitated salts and other solids species (sludge), and a vapor phase associated with the headspace of process vessels. Mercury reactions in the complex-alkaline environment has resulted in the presence of solid, liquid (elemental), vapor, and dissolved mercury species. Over the past two years, there has been an intense effort to understand the chemistry of mercury within the process to determine impacts on the final waste forms. These results revealed that the mercury is present in the elemental state, solid phase, soluble ionic mercury complexes, and methylated species in both the vapor and aqueous phases. Within the aqueous phase organic mercury is the predominant form in several of the process vessels.

Analytical results from the salt solution and sludge indicate that as the high level radioactive sludge is vitrified into glass for final disposal, mercury is currently being recycled within the process and non-volatile mercury species are concentrated by the evaporator systems. Consequently, mercury concentrations are increasing in the salt solution. This is impacting the final radioactive waste form of this material - a solid concrete matrix called saltstone. The presence of organomercury significantly reduces the effectiveness of mercury removal processes built into the system and increases the leachability of mercury from the final disposition waste form. Strategies for the management of organic mercury are being developed to prevent long-term impacts to the disposal of the liquid waste.

TP-137

EVALUATION OF TOTAL MERCURY LEVELS IN THE ENVIRONMENTAL SAMPLES (SOILS) FROM DIFFERENT SITES IN LIBYA

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Mercury is well known as being a toxic element causing significant damage to the human beings and environment. The aim of this study is to investigate the level of mercury exposure to environment and human beings and to establish the local background levels of total mercury in Libya. Soil T-Hg concentrations were measured in 30 soil samples using CV AFS. The local background average value for T-Hg in un-contaminated soils (n = 17) was established (0.043 µg g-1). Moreover, a mercury result from contaminated soil samples (n=13) in both study areas (Around Sirte Oil Company in El- Brega area in the east of Libya and in and around Tripoli city near Abu- Kammash Chlor-alkali plant in the west of Libya) revealed values ranging from 0.92 to 8.52 µg g-1 (mean 4.48 µg g-1). The high mercury content is indicative of the random use of Hg and the lack of control in using this element in the process of amalgamation in Abu-Kammash Chlor-Alkali plant and gas plant in Sirte Oil Company in El- Brega city. This is leading when released in the Mediterranean Sea to an increase in the load of particulate material with long particles time (long residence time), which is accumulated and magnified in the aquatic food chain and is the major exposure route to humans. Mercury has long-range atmospheric circulation and transportation. Throughout its circulation through the atmosphere, Hg can enter the aquatic environment through diffuse and point sources. Me-Hg is taken up by fish; therefore consumption of this fish will increase the human risk.

2I: Safe and reliable handling of mercury in science & technology

TP-138

DIRECT DETERMINATION OF TOTAL MERCURY IN PHOSPHATE ROCK USING IN SITU ALKALINE FUSION DIGESTION.

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Mercury (Hg) is known to be widely distributed in nature, and the average amount of it in the Earth's crust ranges between 15 and 500 ng g-1. Mercury determination in rocks poses major problems, because its abundances are generally extremely low.

The aim of this work was to develop a new method to determine the Hg concentrations in phosphate rock using a dedicated analytical instrument (the DMA80 Tricell by Milestone) that employs an integrated sequence of thermal decomposition followed by catalyst conversion, amalgamation and atomic absorption spectrophotometry. However, releasing the mercury totally from this material is a challenge because hot temperatures are required. When phosphorite and apatite rocks are investigated with a classic thermal decomposition treatment that complies with US EPA method 7473. Therefore, to improve the recovery of total Hg, we performed alkaline fusion digestion (AFD) directly inside the furnace of the instrument, using BCR(32) as a certified reference material (Moroccan phosphate rock – phosphorite). The salts used for the AFD were a mixture of Na2CO3, K2CO3 and Li2CO3, which melt at about 400°C, due to their ability to form a ternary eutectic and to decompose the phosphorite matrices at 700°C. By adopting this analytical approach, the Hg recovery in BCR(32) was about 100%, compared to 40% when the reference material was analysed without using the alkaline fusion salt. We suggest that the AFD allowed the decomposition of the sample matrix and that some Hg compounds linked with other functional groups may be transformed in carbonates that sublimate at lower temperatures than other Hg compounds.

This original method was tested on a number of different geological samples to compare the differences between the AFD method and the thermal treatment in order to verify the working range and to check the robustness of the new approach. This method would be an important step ahead in the Hg speciation studies in phosphate rock samples.

TP-139

PROTOCOL FOR THE SAFE REMOVAL OF DENTAL MERCURY - PROTECTING THE PATIENT AND THE ENVIRONMENT

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The Treaty vs. the Reality - Mercury Free Dentistry the time is now

Dental mercury amalgam is one of the top mercury containing products used in the world and is listed as a phase down product in the Minamata Convention [1]. Mercury from the dental sector has many pathways into the environment, through respiration, cremation, burial, and human waste; however, the largest contributor of mercury into the wastewater comes from the dental offices. New regulations have been passed by the Environmental Protection Agency (EPA) to mandate mercury amalgam separators throughout the United States to capture the mercury waste at its source [2].

In 2004, the estimate of practicing dentists worldwide was approximately 1.8 million [3]. Research shows that dental workers are exposed to mercury through removing and placing fillings, polishing restorations, and handling the mercury waste [4]. We have developed a comprehensive technique and protocol for the safe removal of dental mercury and replacement with non-mercury alternatives. These methods can be utilized in developing countries, countries with emerging economies, as well as developed countries.

According to Sahani et al. (2016) exposure to the high levels of mercury from dental amalgam can lead to serious health effects among the dental health care workers [5].

Mercury has been found to be a causative agent of various sorts of disorders, including neurological, nephrological, immunological, cardiac, motor, reproductive and even genetic. Recently heavy metal mediated toxicity has been linked to diseases like Alzheimers, Parkinsons, Autism, Lupus, Amyotrophic lateral sclerosis, etc. [6].

Multiple studies have shown that occupational exposure to dental mercury is negatively impacting the health of dentists and dental workers. Dental assistants with high exposures to mercury were less fertile than the controls according to Rowland et al. (1994) [7].

In early December 2016, the three major regulatory institutions in Europe, specifically, the European Council, Commission, and Parliament have recommended a ban on mercury dental fillings in children under the age of 15 and pregnant and breast-feeding women as of 2018 [8].

The treaty has created guidelines and recommendations for the Partys actions for the safety and protection of dental personnel, patients and the safe handling of environmental waste created from this source. Our protocol will be able to assist all countries in the early implementation and the elimination of mercury dental amalgam in a safe, environmentally sustainable way.

3a: Risk/benefit communication related to fish and seafood consumption

TP-142

DEVELOPING A FISH CONSUMPTION ADVISORY FOR PREGNANT WOMEN IN THE CARIBBEAN

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Introduction: Fish is a traditional and essential element in the diet of most Caribbean people. However, fish contains methylmercury which is a toxic substance. There are concerns for prenatal exposure to mercury as a result of maternal fish intake. Previous studies conducted in the Caribbean showed where placental mercury concentration was influenced by maternal fish intake. The aim of this study was to develop a fish consumption advisory for pregnant women in the Caribbean. The purpose of the advisory was to promote the 'safe' consumption of fish during pregnancy, in order to prevent high levels of mercury exposure to the fetus.

Method: Food Frequency Questionnaires were administered to a selected group of pregnant women in Jamaica (N= 180) and Trinidad & Tobago (N=80). The participants were asked to recall their average fish consumption within the last three months. The questionnaire included questions on 12 fresh fish and 4 canned fish known to be commonly consumed in both countries. Placenta samples were also collected from each participant and analysed for mercury.

Results: The mean maternal fish intake was 245 grams per week. The highest daily fish intake was found among women who were older than 36 years. The average frequency of maternal fish consumption was 2- 3 times per month in Jamaica and once per month in Trinidad & Tobago. The main category of fish species consumed in Jamaica and Trinidad & Tobago were reef finfish (48%) and large offshore pelagic (37%) *respectively*. The range for placenta mercury concentrations was 0.5 to 7.3µg/kg. Those participants who reported to regularly eat large offshore pelagic fish resulted with the highest placenta mercury concentrations.

Conclusion: The placental mercury concentrations were found to be below the EPA's reference limit derived for prenatal exposure. Therefore, an average maternal fish consumption of at least 245 grams per week is within acceptable safe limit. Pregnant women are advised to eat reef finfish for 2-3 times per month and limit intake of large offshore pelagic fish to once per month. Maternal age should also be considered when developing a fish consumption advisory. This advisory was important to reduce mercury exposure from fish intake, while sustaining the traditional diet of Caribbean people.

TP-143

THREATS TO FRESHWATER SUBSISTENCE FISHERIES FROM HG CONTAMINATION: GLOBAL VARIATION AMONG SITES AND SPECIES

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River and lake fisheries are a critical source of nutrition for hundreds of millions of people worldwide. Contaminant research often focuses on recreational catches in wealthy countries, but the health impact of mercury (Hg) and other pollutants on subsistence consumers who lack dietary alternatives are likely to be more profound. We analyzed multiple species from different feeding guilds in 15 fisheries spanning four continents to assess the degree of health threat posed by Hg bioaccumulation in food webs. These lakes and rivers covered a wide range of land use, water quality, and suspected Hg sources. Average total Hg concentrations in muscle samples varied by two orders of magnitude across sites, including both unusually low (less than 10 ng g-1 dry weight) and high (greater than 1000 ng g-1 dry weight) concentrations. Comparisons among species within and across sites suggest inconsistent effects of fish body size and trophic guild on Hg bioaccumulation, which complicates the development of consumption guidelines based on fish traits. Notably, even small fish in some regions are sufficiently contaminated by Hg to raise health concerns for occasional consumers, and detrimental impacts on children who eat these fish daily are highly likely. Our initial survey of select sites suggests a strong need for systematic assessments of Hg and other contaminants in temperate and tropical subsistence fisheries, and underscores the challenge of devising generalizable advisory protocols for communities whose food security is rooted in freshwater subsistence fisheries.

3d: Engagement of communities impacted adversely by environmental mercury pollution

TP-144

USING A CONCEPTUAL SITE MODEL IN STAKEHOLDER ENGAGEMENT AND DECISION MAKING AT A MERCURY-CONTAMINATED SEDIMENT SITE: ST. LAWRENCE RIVER AREA OF CONCERN

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Cornwall, Ontario has long been a center of industrial activities, relying upon the St. Lawrence River as a source of freshwater for manufacturing processes and effluent dilution and dispersion. In 1985, the International Joint Commission designated the Cornwall area of the St. Lawrence River as an Area of Concern (AOC) under the Canada-U.S. Great Lakes Water Quality Agreement. In 2005, monitored natural recovery in combination with administrative controls was selected as the risk management approach for three zones of the AOC proximate to Cornwall. A conceptual site model was prepared as a framework for synthesizing over 40 relevant reports and to support diverse stakeholders evaluation of the effectiveness of monitored natural recovery. The conceptual site model details sources of mercury, migration and transformation pathways for mercury, human and ecological receptors that potentially contact or contacted mercury, and exposure pathways by which those receptors are or were exposed to mercury. The goal of the conceptual site model is to accurately convey current conditions within the three zones, with sufficient characterization of the processes acting on the mercury to support stakeholders development of site-specific objectives, goals, targets, and associated monitoring approaches. By organizing extensive and diverse information into the framework of the conceptual site model, it is possible to identify key factors influencing the success of monitored natural recovery, as well as fundamental data gaps that impede demonstration of that success. Multiple lines of evidence indicate that mercury in the sediment of the three zones likely poses negligible risks to human health and the environment. Detectable decreases in sediment concentrations are difficult to discern, however, due to inconsistent sampling locations over time, limited sediment core data, and continuing inputs of mercury to the river. For example, storm sewers and combined sewer overflows appear to continue to convey mercury from upland sources to the river. Once all sources of mercury have been mitigated to the greatest extent possible, ongoing monitoring will be necessary in order to determine the effectiveness of monitored natural recovery. Monitoring will demonstrate whether surface sediment mercury concentrations have changed over time and whether it is likely that concentrations consistent with upstream can be achieved in the future.

3f: Methylmercury toxicokinetics and toxicodynamics: human and animal models

TP-145

GENETIC VARIATION IN ABC-TRANSPORTERS MODIFY METHYLMERCURY DISPOSITION

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Methylmercury (MeHg) metabolism differs between individuals and may explain differences in MeHg susceptibility. One explanation for this variation might be that genetic pre-disposition affecting MeHg kinetics can result in individual differences in MeHg body burden despite similar MeHg intake. The glutathione (GSH) pathway has a central role in MeHg metabolism since GSH-MeHg conjugation is a prerequisite for elimination of MeHg from target organs and the body. GSH-MeHg transport occurs via ATP-binding cassette (ABC) transporters, also known to act as multidrug resistance-like proteins. ABC transporters have been associated with MeHg metabolism and toxicity in experimental and animal models, and there is also recent evidence for a role for ABC transporters in MeHg transport in humans. In studies of mother-child cohorts from Italy, Greece and Spain, we found that the childs genotype having single nucleotide polymorphisms (SNPs) in the ABC transporters ABCB1, ABCC1 and ABCC2 can modify the association between maternal fish intake and child MeHg levels (measured in cord blood). Consistent results were found in a Seychellois mother-child cohort in which we observed associations of SNPs in ABCB1, ABCC1 and ABCC2 with maternal MeHg (measured in hair), with one SNP in the ABCC1 gene also showing association with child neurodevelopment. These human studies support the experimental animal models that ABC transporters play a major role for the kinetics of MeHg in the body. Moreover, variation in ABC genes may influence the MeHg dose in the developing child and thus could be relevant to neurodevelopmental outcomes.

TP-146

ALTERNATIVE TESTING METHODS: COMPARING TEST SENSITIVITIES BETWEEN FISH EMBRYO AND FISH CELL MODELS

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Mercury is an intensely studied element and compound family. Regulations pertaining to environmental concentrations, occupational exposures, and dietary consumptions should be scrutinized and refined as the state of the art progresses. The Tox 21 initiative challenges the scientific community to progress to methods that are at once, higher throughput, less consumptive of animal life, and more sensitive than classical toxicity testing methods. In current standard methods apical endpoints used for zebrafish embryos (coagulation, somite formation, and tail detachment) are often surrogates for mortality. Basic biochemical assays, when used in concert, may form the basis of a more sensitive and informative series of endpoints than measures that are stand-ins for mortality. In addition, there is a need to compare in vitro and in vivo results. Here, a systems approach was taken to assess methylmercury toxicity using enzyme activities as indicators of redox stress in both a zebrafish (Danio rerio) embryo model, and a zebrafish derived liver cell line (ATCC CRL-2643). Zebrafish cells were exposed to a range (0.01 μM to 1 μM) of methylmercury-chloride. A similar design was used to expose zebrafish embryos to aqueous methylmercury-chloride (0.01 μM to 10 μM). Current standard endpoints (OECD TG 236) were assessed along with a battery of biochemical assays. Enzymatic activity assays performed in vitro and in vivo included monoamine oxidase, superoxide dismutase, catalase, glutathione peroxidase, glutathione reductase, peroxiredoxin, thioredoxin reductase, and oxoglutarate dehydrogenase. Uptake by embryos and cells was quantified by using GC-CVAFS, and direct mercury AA. In vitro model results were compared to in vivo exposure of zebrafish embryos to similar concentrations of methylmercury. A comparison of the sensitivity of endpoints between standard test methods and the biochemical endpoints will be discussed. Further discussion will include the responses of in vitro exposures using these biochemical endpoints in contrast with in vivo responses. These studies are expected to narrow the gap between mercury in vitro models and in vivo observations in teleost fish. Future work will include studies investigating the effects of exposure among three forms of mercury: inorganic mercury, methylmercury-chloride and methylmercury-cysteine.

TP-147

METHYLMERCURY-INDUCED OXIDATIVE DAMAGE IN LIVER, KIDNEY AND BRAIN OF RATS: PROTECTION BY N-ACETYL CYSTEINE AND SELENIUM

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Methylmercury is a ubiquitous and hazardous material in the environment due to the circulation of inorganic mercury in the environment which is dissolved into rivers and sea, condensed through the food chain, ingested by humans, and consequently affects human health. Therefore, methylmercury deserves the attention of environmental health experts. It is an emerging problem in the world as its concentration is rising continuously due to increased industrial, medicinal and domestic uses. It is bio transformed to highly toxic free metabolites thus eliciting tissue and blood biochemical alterations and oxidative stress. The aim of present study describes the protective effect of N-acetyl cysteine (NAC) either alone or in combination with selenium against chronic mercuric chloride poisoning. The experiment was carried out in male albino Sprague Dawley rats (N=30) which was divided into five groups. Group 1 served as control were received vehicle for twelve weeks (once daily for 7 days). Groups 25 were administered methylmercury (MeHg: 1.0 mg/kg, p.o.) for twelve weeks (once daily for 5 days), group 2 served as experimental control. Animals of groups 3, 4 and 5 were received N-acetyl cysteine (NAC: 0.6 mg/kg, i.p.) and selenium (Se: 0.5 mg/kg, p.o.) and NAC with Se in combination for twelve weeks (after toxicant administration for remaining 2 days only). Chronic MeHg exposure altered various biochemical parameters, including transaminases, alkaline phosphatase, lactate dehydrogenase, bilirubin, gamma-glutamyl transferase, triglycerides and cholesterol, urea, creatinine, uric acid and blood urea nitrogen contents with concomitant decline in protein and albumin concentration in serum. In addition, a significant rise in lipid peroxidation level and mercury ion concentration with concomitant decrease in reduced glutathione content and the antioxidant enzymes activities of superoxide dismutase, catalase, glutathione reductase, glutathione peroxidase and glutathione-S-transferase after chronic MeHg exposure. Results of the present investigation clearly showed that combination therapy with NAC+Se provide maximum protection against chronic mercury toxicity than monotherapy (alone treated groups) by preventing oxidative degradation of biological membrane from metal mediated free radical attacks. The activities of comet assay and MTT assay significantly recovered the damage towards normal after combined treatment (NAC+ Se). Biochemical data were well supported by histopathological findings. In conclusion, combination therapy may be an ideal choice for long term mercury toxicity and oxidative stress.

TP-149

MERCURY-INDUCED EPIGENETIC TRANSGENERATIONAL INHERITANCE OF ABNORMAL NEUROBEHAVIOR IS CORRELATED WITH SPERM EPIMUTATIONS AND DYSREGULATED BRAIN AND RETINA GENE EXPRESSION IN ZEBRAFISH

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Methylmercury (MeHg) is a ubiquitous environmental neurotoxicant. Developmental exposure of zebrafish to MeHg is known to alter their neurobehavior in a manner similar to other vertebrates. The current study investigated the direct and transgenerational effects of MeHg, at tissue doses similar to those detected in exposed human populations, on neurobehavior (i.e., visual startle and spontaneous locomotion), sperm epimutations (i.e., differential DNA methylation regions [DMRs]), and transcriptomics in zebrafish, an established human health model. F0 generation embryos were exposed to MeHg (0, 1, 3, 10, 30, and 100 nM) for 24 hours ex vivo. F0 generation control and MeHg-exposed lineages were reared to adults and bred to yield the F1 generation, which was subsequently bred to the F2 generation. Direct exposure (F0 generation) and transgenerational actions (F2 generation) were then evaluated. Hyperactivity and visual deficit were observed in the unexposed descendants (F2 generation) of the MeHg-exposed lineage compared to control. An increase in F2 generation sperm epimutations was observed relative to the F0 generation. Investigation of the DMRs in the F2 generation MeHg-exposed lineage sperm revealed associated genes in the neuroactive ligand-receptor interaction and actin-cytoskeleton pathways being effected, which correlate to the observed neurobehavioral phenotypes. Analysis of dysregulated genes revealed via sequencing of total RNA isolated from F2 generation MeHg-exposed zebrafish retina and brain (compared to control) showed significant enrichment in pathways associated with vision, circadian rhythm, and neurological disorders. Collectively, this evidence supports that developmental MeHg exposure can induce epigenetic transgenerational inheritance of abnormal neurobehavior correlated with dysregulated brain and retina gene expression and sperm epimutations in F2 generation adult zebrafish. Therefore, mercury has the ability to promote the epigenetic transgenerational inheritance of disease in zebrafish, which significantly impacts its environmental health considerations in all species, including humans. Further study of the transgenerational health effects of MeHg is required to better understand the risks for human populations, which, if transgenerational effects are ignored, are dramatically underestimated.

TP-151

PHYSIOLOGICALLY-BASED PHARMACOKINETIC MODELING OF METHYLMERCURY IN YOUNG RINGED SEALS

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Methylmercury (MeHg) is a potent, bioaccumulative neurotoxicant that is particularly harmful to mammals at early developmental stages. Previously published studies have measured concentrations of MeHg in young ringed seals but have made little effort to quantitatively explain variability in the data. We constructed a physiologically-based pharmacokinetic model to examine the relative importance of body growth, changing diet, and internal demethylation to explain changes in MeHg burdens in various biological compartments. The model is evaluated with measured MeHg and total mercury (Hg) concentrations in young-of-the-year ringed seal tissues from Labrador, Canada that were harvested between 2012 and 2015. Most seals were less than one year of age. Measured mean Hg concentrations (wet weight) in muscle and tissues from 52 individuals were: 0.095 mg/g (n = 52, s = 0.081 mg/g), and 0.67 mg/g (s = 1.06 mg/g), respectively. Mean MeHg concentration (wet weight) in muscle was 0.11 (n = 35, s = 0.089 mg/g) and is 0.12 mg/g (n = 52, s = 0.15 mg/g) in liver. Model outputs show that the dynamics of mercury disposition and accumulation in the first year can be largely attributed to dietary shifts. This model can be further modified and applied to other marine mammals to study early-life exposure patterns for species of interest, including those consumed as country foods by Inuit communities in Arctic and Subarctic regions.

TP-152

THE EFFECTS OF METHYLMERCURY ON BREAST CANCER CELLS

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Metalloestrogens are small ionic metals that activate the estrogen receptor (ER). Studies have shown that when metalloestrogens bind to the ER, there is an increase in transcription and expression of estrogen-regulated genes, which induces proliferation of estrogen-dependent breast cancer. Methylmercury (MeHg), a metalloestrogen, is present in the environment and is toxic at moderate to high concentrations. However, at lower concentrations MeHg may promote the proliferation of ER-positive breast cancers and protect cells against pro-apoptotic signals. To investigate the effects of MeHg treatment on breast cancer cells in vitro, MCF7 breast cancer cells were treated with concentrations of MeHg ranging from 1 nM to 100 mM. MeHg analysis was used to quantify intracellular mercury concentrations and cell proliferation and apoptosis were determined by cell counting and Annexin-V staining, respectively. We defined a protocol that maximizes cellular exposure to mercury and we found that treatment of human ER-positive breast cancer cells with 1 nM MeHg promoted proliferation, while treatment with a concentration of 100 nM induced apoptosis. Investigations into the effects of dietary MeHg treatment of zebrafish on breast cancer growth and progression are currently underway. Clarifying the effects of MeHg on breast cancer will improve our understanding of how environmental toxins affect tumor progression and may lead to the development of future therapeutic strategies.

TP-153

IMPACT OF METHYLMERCURY IN HYPOSTOMUS GYMNORHYNCHUS AND HOPLIAS AIMARA HARVESTED IN PRISTINE AND CONTAMINATED SITES FROM THE OYAPOCK RIVER IN FRENCH GUIANA

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A multidisciplinary approach has been conducted to compare toxicity mechanisms of methylmercury (MeHg) previously obtained in zebrafish (Danio rerio) during experimental condition to those obtained in fish harvested in the field in French Guiana. For this purpose, genes known to be involved in antioxidant defences, metal chelation, active efflux of organic compounds, mitochondrial metabolism, DNA repair and apoptosis have been cloned and characterized for two typical fish: Hypostomus gymnorhynchus (a grazer fish) and Hoplias aimara (a top predator). Fish were obtained from three different sites; a pristine site (3 sauts) and two mercury-contaminated sites (Oyapock and Camopi). Expression levels were determined on brain, muscle and liver as well as ultrastructural analyses by electronic microscopy. Moreover, quantification of mercury bioaccumulation and of metallothionein (MT) proteins have been done in the same tissue. Results obtained for H. gymnorhynchus evidenced that genes involved in detoxification, oxidative stress response and mitochondrial metabolism were overexpressed in contaminated sites compared to pristine one in all the tissue. Histological analyses showed that damages in mitochondria were also observed in fish from the contaminated sites. Indeed, in contaminated muscles a decrease of the inter-bundle surface, mitochondria with variable shapes, sizes and cristae disorganization, also decreasing the surface area and inter-bundle surfaces were observed. In liver from the contaminated fish, an increased quantification of MT levels were evidenced. All these results confirmed those obtained in laboratory-controlled experiment with D. rerio.

TP-154

TOXICOKINETICS OF MERCURY IN THE HUMAN PLACENTA: PRELIMINARY DATA ON RELATIONSHIPS BETWEEN GENOTYPE AND PHENOTYPE IN HEALTHY AND DISEASED PLACENTA

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Although it has been known for decades that the organic compound methyl mercury (MeHg) is neurotoxic and passes the placenta unhindered, our knowledge of the transport mechanisms is extremely low.

The placenta is a transient organ that persists just nine months but has a significant influence on health and development of the offspring. Dysfunction of the placenta often leads to pregnancy complications such as gestational diabetes (GDM), pre-eclampsia (PE), and intrauterine growth retardation (IUGR).

The development of placental dysfunction is multifactorial. The placenta is well suited for the investigation of genotype-phenotype associations because the organ is easily available, protein expression and function are readily measurable, and primary cells can be isolated therefrom.

In preliminary studies, we have investigated which proteins are involved in placental toxicokinetics (transport and metabolism) of mercury. A number of these proteins are also involved in placenta dysfunctions. They include system L amino acid transporters, enzymes of the anti-oxidative glutathione system and efflux transporters from the family of ABC transporters.

The main questions are: Which proteins are involved in placental dysfunction? To what extent does the genetic background (sequence variants) explain abundance or activity of these proteins? Is the infant genotype linked to the placental phenotype?

In total 170 mother-child pairs (100 healthy, 70 with GDM, PE, IUGR) will be genotyped. Expression and activity of the candidate proteins are examined in healthy and dysfunctional placentas using MeHg as a model substrate. By researching placental mercury toxicokinetics, we gain insights that are not only relevant for reproductive toxicology, but also contribute to a better understanding of the individually different placenta (patho) physiology. The aim is to identify genetic variants predisposing to pregnancy complications. The identification of such genetic markers is a very big step towards individual treatment and counselling during pregnancy. Preliminary data on selected candidate proteins will be discussed.

TP-155

CHARACTERIZATION OF MERCURY-BINDING PROTEINS IN RAT BLOOD

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Blood proteins play important roles in mercury transport, toxicity and metabolism. Characterization of mercury-binding proteins, especially proteins with low abundance is critical for understanding their trafficking and underlined mechanisms of toxicity. Till now, very limited proteins, i.e., albumin, 2-macroglobin, and transferrin had been identified as mercury-binding proteins in plasma. For erythrocyte, hemoglobin was the only protein known to associate with mercury. In this study, mercury-binding proteins in rat plasma and erythrocyte were characterized in vitro by continuous flow gel electrophoresis coupled with inductively coupled plasma mass spectrometry (GE-ICP-MS). It was found that most of Hg were associated with proteins, in which around 60% of mercury was bound to albumin and 25% to hemoglobin. Apart from the high abundance proteins, ten mercury-binding proteins with low abundance in blood were identified. There were four proteins in plasma, which were glutathione peroxidase 3, apolipoprotein E, alpha-1-antiproteinase, and transferrin, respectively. For erythrocyte samples, six mercury containing proteins were detected. Mercury preferentially binds to hemoglobin (8 %) followed by peroxiredoxin-2 (5 %), while the other three proteins bound 3 % mercury respectively. Our finding provided useful information to further investigate health effects and toxicities related to Hg exposure.

TP-156

DIFFERENT EFFECTS OF METHYLMERCURY EXPOSURE ON LOCOMOTOR BEHAVIORS IN ADULT MALE AND FEMALE ZEBRAFISH (DANIO RERIO)

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Methylmercury (MeHg) is a widely distributed environmental neurotoxin with established effects on the central nervous system, yet the subtle behavioral effects of MeHg toxicity are less well studied. Previous work from this group has demonstrated that MeHg exposure disrupts locomotor behavior in adult male mice, specifically behaviors related to coordination, balance and strength. Other groups have shown that the deleterious effects of MeHg can be prevented in male mice with estrogen treatment, suggesting a sex difference in susceptibility to MeHg toxicity. The goal of the present study is to further examine sex differences in MeHg-induced behavioral changes using an aquatic animal model. This study investigated the impact of MeHg exposure on several swimming behaviors in adult male and female zebrafish. MeHg was administered daily in food over a three-week period. The daily MeHg dose (0.1 ug/g/day) was comparable to known environmental exposure levels. Swimming behaviors (swim distance, swim speed and line crossings) were assessed before treatment and then weekly during the treatment period. Preliminary findings suggest that swimming behaviors were unaffected in female zebrafish exposed to MeHg at this dose. However, MeHg exposure increased swimming activity in males by week three of treatment. Behavioral differences will be linked to changes in antioxidant enzyme activities in tissues. Future studies will focus on the potential neuroprotective effects of estrogen on MeHg toxicity in zebrafish.

TP-158

DEVELOPMENT OF AN ECOPHYSIOLOGICAL DAPHNIA MODEL TO EXAMINE THE INTERACTIVE EFFECTS OF NUTRITION AND METHYLMERCURY TOXICITY

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In spite of efforts to address issues of mercury in the environment, levels continue to rise. Rapid and reliable tools are imperative in water quality management to mitigate potentially catastrophic ecosystem shifts. Through the integration of ecosystem-level models with chemical analysis tools, our research proposes the development of a novel bioindicator technique that will connect the physiological stress of individual organisms to ecosystem dynamics. Daphnia, a crustacean zooplankton, represents an essential compartment in aquatic ecosystems at the autotroph-heterotroph interface, connecting phytoplankton to many fish species, and has been suggested as a keystone species. We have developed a model that aims to elucidate the interactive effects of mercury toxicity and nutrition (in terms of food quality and quantity) on the relationship between phytoplankton and Daphnia through an understanding of both mass and energetic consequences. Generally, zooplankton modelling studies on food quality have examined a limited range of nutrients, typically macronutrients such as carbon, nitrogen and phosphorus; we have expanded our scope of nutrition to include fatty acids, amino acids, saturated fats, and other nutrients. Our model stipulates a physiological hierarchy, prioritizing different physiological processes in the order of neurological functions, bio-energetics, osmoregulatory maintenance, waste management, and growth investments. Daphnia resiliency is controlled by both food quantity and quality and each physiological process is modulated by the somatic levels of different metabolites. With the enrichment of food with congeners associated with neurological and energetic functions (e.g., tryptophan, phosphorus), effects of toxicity can be countered. Our work highlights that healthy dietary patterns can be critical in ameliorating toxicity, and therefore biotic populations cannot be maintained solely through contaminant management. Our modelling framework links physiological and biochemical level processes to ecosystem patterns to provide a deeper understanding of the interactions between toxicity and food quality and whether food quantity and quality can mitigate the impacts of mercury toxicity in Daphnia and improve resistance and resilience against mercury. We offer the prospective of quantitative response indicators in long-term water monitoring efforts and a framework that can accommodate parameterization from values derived through metabolomics experiments. Understanding the responses and linkages between these ecosystem drivers may improve the management and conservation of the ecosystems contaminated with mercury.

TP-159

ELUCIDATING THE BIOCHEMICAL EFFECTS OF MERCURY EXPOSURE IN AN ENVIRONMENTAL SENTINEL WITH METABOLOMICS AND EPIGENETICS TECHNIQUES

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Mercury (Hg) is a toxic environmental pollutant with a ubiquitous, worldwide distribution. The toxic effects of methylmercury (MeHg) exposure are well documented; and include neurodegenerative diseases (e.g. Minamata Disease), muscular disorders, and lowered reproductive success. However, determination of the sub-lethal effects of MeHg exposure is complicated due to the lack of symptoms prior to the onset of degenerative diseases. In an effort to classify some of the underlying biochemical effects of chronic MeHg exposure, we investigated physiological and epigenetic changes associated with two doses of chronic MeHg exposure over a two-year time period on an ecologically important reptilian sentinel, the diamondback terrapin (Malaclemys terrapin). Erythrocyte samples were analyzed for total mercury content and subsequently for global DNA methylation by LC-MS/MS and plasma was analyzed by 1H NMR for metabolomic effects. DNA methylation is a well-studied epigenetic modification that controls gene expression. When DNA methylation patterns are changed, as a result of external stimuli, altered gene expression and dysregulation of certain cellular processes can occur and be characterized. Analyzing the plasma metabolic profile of organisms exposed to MeHg in a controlled setting allows the identification of metabolites and their corresponding pathways that change in response to the exposure. Plasma metabolomic profiles were analyzed by multivariate and univariate techniques across doses, gender, and annual time scales. This study aimed to identify small molecules that change in response to chronic MeHg exposure, as well as investigate changes in epigenetic modifications that are likely exacerbated as a result of exposure. Both of these tools may lend insight to the underlying cellular mechanism of MeHg exposure and allows for a greater understanding of organism-environment interactions.

TP-160

UNVEILING COPING STRATEGIES WITH MERCURY IN AQUATIC AND SEMI-AQUATIC INHABITANTS

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Despite the credible information on environmental hazards identification/characterization, risk assessment and coping strategies in aquatic and semi-aquatic inhabitants, lacunae on mechanistic aspect entangling the previously mentioned issues are perceptible in literature. Thus, the current work aimed to assess mercurys potential toxicity on biota and discusses organisms survival strategies under natural environmental conditions. Primary consumers (bivalve- Scrobicularia plana) were selected since they comprise the baseline of the food web and serve as a conduit for bottom-up energy transfer, whereas the salt marshes plants (Halimione portulacoides and Juncus maritimus) were considered keeping in view their status as essential ecosystem base components. Area chosen for this study was Laranjo Basin, Ria de Aveiro, Portugal, where a well defined mercury gradient has been reported due to chloralkali plant.

In bivalves, inter-age and organ-specific approaches were applied by using different annual age classes (2+, 3+, 4+ and 5+ year old) and assessing specific organs (gills, digestive gland), respectively. Besides total and organic mercury accumulation, endpoints combining lipid peroxidation, as damage sign, and antioxidant protection were determined. It was revealed that the use of whole-body analyses could be particularly compromising when enzymatic antioxidants are addressed. Besides the contribution to understand mercury toxicodynamics, specific organs approach was strongly recommended in order to avoid misinterpretations. Analyses of non-enzymatic antioxidants revealed that the evolution of the adaptive skills of S.plana over time depends on the contamination extent. Hence, under a moderate contamination scenario, the intervention of the different antioxidants (measured in whole-body) took place harmoniously, evidencing an adjustment capacity increasing with the age. In opposition, under a higher contamination degree S.plana failed to efficiently cope with mercury threat.

Salt marsh plants H. portulacoides and J. maritimus exhibited the highest and the least mercury-remediation/accumulation potential, respectively. Salt marshes dominated by J. maritimus exhibited a stronger capacity to retain and phytostabilize mercury in belowground than those dominated by H. portulacoides. Conversely, extensively H. portulacoides-colonized salt marshes are expected to translocate more mercury to aboveground parts. It can be possible to phytostabilize metals in rhizosediments (using J. maritimus) or phytoextract metal by accumulating in aboveground plant tissue for subsequent plant removal (using H. portulacoides). Moreover, mercury-induced oxidative stress was differentially counteracted by ascorbate-glutathione cycle-components in the studied plants. These changes were strongly substantiated with the changes at proteome level. Conclusively, coping strategies in both animal and plant revealed their significance as biomarkers for environmental hazards safety screening.

TP-162

THE BIOCHEMISTRY OF THE FIVE "SOS" MECHANISMS OF MERCURY TOXICITY

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Methylmercury (MeHg) toxicity is characterized by: 1.) long latency of onset of symptoms following toxic exposure, 2.) neurological tissue specificity of pathological effects, 3.) inhibition of selenoenzymes in brain tissues, 4.) oxidative damage in the affected tissues, 5.) accentuated fetal vulnerability, and, 6.) preventative/rescue effects accompanying supplemental dietary selenium (Se) commonly referred to as the Se-protective effect. These aspects had previously been difficult to explain, but understanding of MeHg toxicology has improved tremendously in the past decade. Since we now recognize that Hgs affinity for selenium (Se) is ~1 million times greater than its affinity for sulfur, its second best binding partner, it has become obvious that Se, not sulfur, is the molecular target of MeHg toxicity. Because of its high binding affinity for Se, MeHg inhibits synthesis and activities of Se-dependent enzymes that are required for the health, function, and development of brain tissues. The 25 genetically distinct and functionally elite enzymes expressed in humans perform essential functions in brain physiology including; preventing and reversing oxidative damage to lipids and proteins, enabling DNA synthesis, and regulating thyroid hormone metabolism, calcium homeostasis, and cell signaling pathways. The toxic effects of high MeHg exposures arise from its unique abilities to selectively and irreversibly inhibit selenoenzyme activities. This understanding MeHgs effects provides a unifying perspective that consistently explains all aspects of MeHg toxicity. The involvement of Se-physiology in mechanisms of MeHg toxicity were not initially recognized because selenoenzyme metabolism and its unique roles in brain and endocrine tissues were generally unknown. However, in recent years, the Se-dependent aspects of their physiology are becoming better understood. As a result, the characteristic features of MeHg toxicity have become much easier to understand. High MeHg exposures occur through a sequence of biochemical reactions referred to here as SOS mechanisms. These include; Synergies of Sequestration (SOS-1), Silencing of Selenoenzymes (SOS-2), Sequestration of Selenium (SOS-3), Suicide of Selenium-Deprived Cells (SOS-4) and Sustained Oblivion of Sec Synthesis (SOS-5). These disruptions have consequences that increase in severity as tissue MeHg concentrations approach, and especially as they exceed equimolar stoichiometry with tissue Se. The effects of SOS mechanisms on Se physiology and biochemistry coincide with features of MeHg toxicity which were previously difficult to explain. Predictions based on these mechanisms coincide with observations in cell culture and animal models as well as in epidemiological studies of the effects of MeHg exposures on neurodevelopmental and cardiovascular outcomes.

TP-163

PROTEOME OF PRIMARY ASTROCYTES INDICATE A CENTRAL ROLE OF OXIDATIVE INJURY EXPOSED BY MEHG

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Methylmercury (MeHg) is a neurotoxicant that posed a health risk in both wildlife and human. Cerebellum is the main target of mercury toxicity. The toxic effects of MeHg on specific brain cell type is still unclear. In this study, cerebellar primary astrocytes were analyzed for cellular reactive oxygen species (ROS), total Hg accumulation, and whole cell proteome after exposed with MeHg (1 µM and 5 µM) for 24 hours. ROS and intracellular Hg concentrations showed a dose-dependent increase ($p<0.05$). In proteomic analysis, a total of 3230 proteins were identified, among them 436 proteins were significantly changed (One Way ANOVA, $p<0.05$). Biological processes enrichment analysis showed that small molecule metabolic process, energy derivation by oxidation of organic compounds, cellular respiration, oxidation-reduction process and positive regulation of DNA biosynthetic process are the main functions affected by MeHg. Oxidation-reduction process is the most significantly changed category with 75 proteins were involved. After correction of the p value (Permutation-based FDR method), only 17 and 35 proteins were differentially expressed in 1 µM and 5 µM exposed MeHg, respectively. Oxidoreduction coenzyme metabolic process was significantly changed in both treatment groups. Oxidoreductase complex, mitochondrial respiratory chain, and membrane raft are the main celluar components affected in 5 µM MeHg but not in 1 µM MeHg ($p<0.05$). KEGG Pathway analysis showed Huntington's disease (HD) was enriched ($p<0.05$) in 1 µM MeHg exposed astrocytes, which is further confirmed our previous publication on a MeHg dosed marmoset model. These results indicated that oxidation and reduction process is a major event occurred in MeHg exposed astrocytes. MeHg exposure was associated with neurodegenerative disease such as HD. Increasing dose of MeHg can disrupt energy generation which is evidenced by the significant changes of mitochondrial respiratory chain system.

TP-164

EFFECTS ON PROLACTIN (PRL) ON CYTOTOXITY INDUCED BY METHYLMERCURY IN HUMAN LYMPHOCYTES AND HUMAN PROMYELOCYTIC LEUKEMIA CELL HL60, BOTH IN VITRO.

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Mercury is a xenobiotic metal that is a highly deleterious environmental pollutant. The biotransformation of mercury chloride (HgCl2) into methylmercury chloride (CH3HgCl) in aquatic environments is well known and humans are exposed by consumption of contaminated fish, shellfish and algae. Methylmercury has been an environmental concern to public health and regulatory agencies for over 50 years because of its neurotoxicity. Its association with nervous system toxicity in adults and infants near Minamata Bay, Japan, in the 1950's initiated environmental health research inquiries that continue to this day. The objective of the present study was to determine the changes induced in vitro by two mercury compounds (HgCl2 and CH3HgCl) in cultured human lymphocytes; and after that evaluate Prolactina's action (PRL) on the organomercurial (CH3HgCl) activity in human lymphocytes and human promyelocytic leukemia cell HL60, both in vitro. The cultures were incubated to 37ºC for 48 h for both biological systems and the treatments were realize 9h after the beginning stimulating cells. A significant increase ($P < 0.05$) in the relative frequency of chromosome aberrations was observed for all concentrations of CH3HgCl (1, 10, 100, and 1000 µg/l) when compared to control, whether alone or in an evident sinergistic combination with HgCl2. In the second experimental block, CH3HgCl when alone treaty (50, 100, 500 and 1000 µM) it was cytotoxic also, however its reduced when treaty together with PRL (1,10 and 100 nM). The frequency of polyploid cells was also significantly increased ($P < 0.05$) when compared to control after exposure to all concentrations of CH3HgCl alone or in combination with HgCl2, however reduced been in PRL presence. CH3HgCl significantly decreased ($P < 0.05$) the mitotic index at 100 and 1000 µg/l alone, and at 1, 10, 100, and 1000 µg/l when combined with HgCl2, showing a synergistic cytotoxic effect, the same results presented in the second experimental block too, however the PRL presents a protector effect over that. Our data showed that low concentrations of CH3HgCl might be cytotoxic/genotoxic and the PRL is a potent antimutagenic agent in this biological systems.

TP-165

TOXICOKINETICS OF MERCURY DEMETHYLATION: MERCURY ACCUMULATION AND SPECIATION IN THE LIVERS OF MARINE AND FRESHWATER FISH SPECIES

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Mercury is a global contaminant that is atmospherically deposited from a variety of anthropogenic and natural sources. In aquatic systems, bacteria convert inorganic mercury (Hg (II)) into the more bioaccumulative and toxic form methylmercury (MeHg). Fish store mercury mainly in muscle, liver and kidney tissues. In the liver, MeHg is metabolized (demethylated) to form Hg (II). In many fish species, it is unknown if there is a threshold concentration at which demethylation occurs or whether demethylation is rate limited. It has been postulated that phylogenetic differences among fishes in immune organization may determine demethylation potential and thus the ability of a species to distribute mercury amongst tissues. The objective of this study was to examine mercury accumulation and speciation in several marine (n= 12) and freshwater (n=14) fish species. Liver and muscle tissue samples were taken and total mercury concentrations determined using a Milestone DMA-80 direct Hg analyzer. Toluene extraction or GC-CVAFS was used to remove MeHg from liver tissues and determine concentrations of MeHg and Hg (II). A percent MeHg was calculated for each individual as well as a ratio of total muscle mercury to total liver mercury as a proxy for examining sequestration tissues. Mean total muscle Hg concentrations across all species ranged from 0.28 (Ladyfish) 5.00 (Bowfin) mgkg dw, and mean total liver Hg ranged from 0.24 (Bonnethead) 13.51 (Spotted Gar) mgkg dw. The highest concentrations for both muscle and liver were seen in freshwater species. Liver total Hg was positively correlated with liver MeHg for salmonids, whereas for all other species, there seems to be a threshold effect. Our results show multiple trends to describe the relationship between liver total Hg and % MeHg. These results will add important information to the knowledge of how phylogeny potentially influences mercury demethylation, and the toxicokinetics of mercury demethylation amongst fishes to help develop a next-generation risk assessment that incorporates species sensitivity.

TP-166

PROTEOMIC AND TRANSCRIPTOMIC INSIGHTS INTO CELLULAR AND MOLECULAR DAMAGE AND RECOVERY FROM INORGANIC AND ORGANIC HG EXPOSURE IN A MODEL MICROORGANISM

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Bacteria are the most vigorous and versatile transformers of Hg in all global ecosystems, some making the very lipid soluble forms, Hg(0) and MeHg(I), and others converting these to highly reactive ionic forms Hg(II) and MeHg(I). Such processes, long studied in the external environment, are increasingly recognized also to operate within commensal microbial ecosystems (microbiota) of humans, and other wildlife exposed to Hg environmentally or iatrogenically. All macroscale Hg transformations have at their base the enzymes within individual cells which catalyze those transformations. Most often those cells are bacterial, simply because they outnumber all other cell forms on Earth and occupy niches in every temperature, humidity, salinity, and oxygen range on the planet, even those with highly toxic metal values.

Knowledge of the many ways in which diverse bacteria are affected by and then transform Hg is essential for understanding the macroscale processes on which environmental remediation, stewardship and risk analyses are based. This is true not only on the scale of terrestrial geology, oceanography, glaciology, atmospheric science, etc but also directly in the plant and animal victims of Hgs toxicity. Surprisingly, there is limited understanding of the distinctly different ways in which inorganic (Hg) and organic (RHg) mercury compounds affect subcellular biochemistry. Most monitoring of exposure to these compounds is by proxies such as behavioral or neurological measures and/or a few signature proteins or metabolites.

Moving our vision to the interior of living cells, we investigate key subcellular targets of mercurials in a common gut commensal, E. coli. Well describe the following studies on growing E.coli cells: (1) biophysical analyses quantifying disruption of electrolyte, metal, and biothiol homeostases by RHg and especially Hg compounds; (2) a novel global LC/MS-MS proteomics method identifying >300 proteins variously vulnerable to stable RHg or Hg modification, many with highly conserved human homologs, especially in mitochondria; and (3) a longitudinal RNA-seq systems level comparison of gene expression showing strikingly different responses immediately after exposure to and during recovery from RHg or Hg compounds. Our findings provide foundations for (a) developing specific biomarkers for RHg/Hg exposure, (b) understanding long-term Hg accumulation in higher vertebrates, (c) investigating the mechanisms of hormesis i.e. use of subtoxic stressors as adaptogens, and (d) assessing nutritional, pharmaceutical or environmental interventions to recruit bacteria in support of recovery from chronic or acute RHg/Hg exposure in individual animals or humans or in external environmental settings.

TP-167

EVALUATION OF NEUROBEHAVIORAL DISORDERS IN METHYLMERCURY-EXPOSED KK-AY MICE BY DYNAMIC WEIGHT BEARING TEST

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Methylmercury (MeHg) is known to cause neurobehavioral disorders in humans and experimental animals. We are studying MeHg toxicity in type 2 diabetic KK-Ay mice to clarify the effect of glucose metabolism disturbance on MeHg toxicity. In a previous study, we observed that exposing 4-week-old KK-Ay mice to 5 mg Hg/kg MeHg resulted in severe neurobehavioral disorders such as hindlimb clasping. Neurobehavioral disorders due to MeHg exposure in rodents have been mostly evaluated by observation of hindlimb crossing, rota-rod performance test, and footprint test. However, it is difficult to quantitatively evaluate the neurobehavioral disturbance of MeHg-treated KK-Ay mice because of their obesity. In this study, we administrated MeHg (5 mg Hg/kg/day p.o.) to male KK-Ay mice three times per week for 5 weeks beginning at 12 weeks of age, and examined neurobehavioral disturbances using the dynamic weight bearing (DWB) test, which has been used to assess pain. MeHg-treated mice began to lose body weight approximately 4 weeks after treatment was initiated. Seven of 9 MeHg-treated mice showed neurological symptoms such as ataxia and gait disturbance in the final stage of the experiment. The weight measured using the DWB test was lower for the forelimb than for the hindlimb before MeHg treatment and until 1 week after treatment was initiated. At weeks 24 of MeHg exposure, the DWB load on the forelimb became similar to that on the hindlimb. After 5 weeks of exposure, the DWB load on the forelimb exceeded that on the hindlimb. Injury of sciatic nerves in MeHg-exposed KK-Ay mice with neurobehavioral disorders was detected using the Masson-Goldner staining. This finding indicates that the DWB test can be useful for semi-quantitative evaluation of neurobehavioral disorders in MeHg-exposed rodents.

TP-168

MATERNAL TRANSFER OF MERCURY IN THE BLOOD OF ORGANISMS STANDING ON THE TOP OF TROPHIC CHAIN

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Marine mammals are exposed to mercury mainly through the diet. Being top predators they accumulate high levels of pollutants as the consequence of biomagnification process. After absorbtion, toxic substances, as methylmercury, are distributed throughout the organism via circulatory system. Blood is an excellent transport channel for methylmercury. Percentage of this form in blood may exceed 90%. Females exposure to methylmercury during pregnancy may be extremely dangerous to the fetus. because physiological barrier such as placenta is transparent for this compound and cannot provide protection against it.

The object of examination was the grey seal (Halichoerus grypus) females and their pups blood. Seals stay in Hel Marine Station (Institute of Oceanography, University of Gdansk, Poland). 4 females located there every year give a birth to pups which after 3 weeks of nursing are being prepared to live independently in their natural environment. After this, all the pups are released to the Baltic Sea due to grey seal reintroduction programme. During 3 years of sampling 9 pups were born in sealarium.

In all blood samples total (HgTOT) and organic (HgORG) myercury concentrations were measured using atomic absorption spectrometer AMA 254. Wherein analysis of the HgORG included its previous extraction and transferring it to a hydrophobic carrier.

The aim of the study was not only checking the relationship between MeHg concentration in seal females and their pups blood, but also the analysis of changes in Hg concentration in females and their pups blood during the first weeks after birth. To verify whether the transfer processes between mother and offspring occur in a similar way in humans, studies were supplemented with the analysis of human blood (women and their newborn children).

This study resulted in statement that lactation period has impact on changes in mercury concentration in maternal as well as offspring blood. Just after delivery, levels of mercury concentrations in blood of pup mother pairs were similar (~25 ng Hgg-1 w.w). The differences started to occur as the experiment progresses. The lowest concentrations in females blood were measured just after labour. In next 21 days of nursing, concentration of mercury in females increased (up to 48 ng Hgg-1 w.w). It was observed that lactation period affected reversely on mercury concentration in pups blood which decreased at the same time (down to 7 ng Hgg-1 w.w).

TP-169

THE INFLUENCE OF LIFE HISTORY AND DIET ON MERCURY BIOACCUMULATION AND BIOMAGNIFICATION IN BLOOD OF BOTTLENOSE DOLPHINS, TURSIOPS TRUNCATUS, UNDER HUMAN CARE

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Physiological and ecological factors, including age, sex, diet, and geographical location can influence mercury concentrations in and among bottlenose dolphin (Tursiops truncatus) populations. Dolphins under human care can represent free-ranging dolphins and account for data variability usually introduced by location, age, unknown diets, and individual feeding preferences. This study examines total mercury concentrations and nitrogen (δ15N) and carbon (δ13C) bulk stable isotopes in whole blood of bottlenose dolphins under human care and their whole prey to determine how life history and diet influence mercury bioaccumulation and biomagnification. This sample set represents the longest ongoing study with the greatest number of animals and samples collected in a controlled setting known to date. Blood samples (n = 199) were collected from 2011 to 2015 from eighteen bottlenose dolphins at Dolphin Quest Hawaii (DQH) and Oahu (DQO) as well as paired prey samples (n = 20). Total mercury was measured by atomic absorption spectrometry (AAS) and bulk stable isotopes were measured by isotope ratio mass spectrometry (IRMS). The average mercury concentration (± SD) in bottlenose dolphin whole blood was 48.1 ± 18.6 ng/g wet mass, which is approximately ten times lower than blood mercury concentrations measured in the Sarasota, Florida wild dolphin population. Sex and age class had a statistically significant influence on dolphin blood mercury concentrations. Adult females had significantly greater mercury concentrations than adult males (p = 0.0039), and pregnant females had lower mercury concentrations than lactating females (p = 0.0274). Calf mercury concentrations were significantly lower than adults (p < 0.0001) and subadults (p = 0.0005). The average daily mercury uptake accounted for all the variability observed among sex and age class. Although mercury concentrations in blood increased on average approximately 3.3 ± 3.8 ng/g wet mass per year, mercury concentrations in whole blood did not increase significantly over time for all animals. This study was also the first to model mercury biomagnification between bottlenose dolphins and their diet in a controlled setting using δ15N measured in dolphin blood and prey. There was a significant positive correlation between log10 mercury concentration and δ15N values in whole blood and prey of adult dolphins (p < 0.0001). The trophic magnification slope (TMS) was calculated between 0.18 and 0.23, which was similar to other observations in marine food webs.

TP-170

FORMATION OF HGSE MICRO-DEPOSITS IN THE EYE AND INTERNAL EAR OF LONG-FINNED PILOT WHALES

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Since the industrial revolution, mercury concentrations in air, water, soil, and living organisms have been on the rise. Methylmercury is the most bioaccumulative form of mercury in the environment. Depending on the level of exposure, effects of methylmercury on wildlife can include mortality, reduced fertility, slower growth and abnormal behavior that affects survival.

The sensory impairments reported in individuals consuming fish high in methylmercury were previously attributed to methylmercury injuring a specific region of the brain. However, recent results (Korbas et al. ACS Chem. Biol. 2013, 8: 2256-2263), which showed preferential accumulation of methylmercury in sensory organs such as the eye, indicate that a more direct damage of specific sensory cells may also take place.

Pilot whales are source of high mercury food for local population in the Faroe Islands and are notorious for stranding themselves on beaches. Several hypotheses have been proposed to account for this behavior, however methylmercury-induced sensory impairment has never been explored in great detail. To verify the sensory toxicity hypothesis, we have investigated mercury and selenium distribution and speciation in the eye (lens, cornea, retina, optic nerve) and internal ear (cochlea, vestibule) of long-finned pilot whales (Globicephala melas) using synchrotron based X-ray fluorescence mapping (XFM) and micro-X-ray absorption spectroscopy (micro-XAS), respectively.

Using XFM and micro-XAS, we have probed several different specimens for mercury, selenium and other metals and metalloids. The mercury distribution and levels significantly varied between tissues. Low levels of mercury were detected in the eye lens, cornea and cochlea. Interestingly, high mercury was always co-localized with high selenium in the form of small (5-10 microns) deposits. Densely distributed HgSe micro-deposits were observed in the vestibular nerve. Similar deposits but with lower spatial density were also mapped in the optic nerve and in the inner nuclear layer of the retina. The HgSe particles had various sizes and Hg:Se ratios. Since in XFM, the spatial resolution of the elemental maps is determined by the size of the X-ray beam (5 microns in this study), those particles could be significantly smaller than a few microns. Currently, using Transmission Electron Microscopy (TEM), we are determining the dimensions and subcellular localization of these micro-deposits. The results of this study will shed more light on methylmercury detoxification pathways and the role of selenium therein. Moreover, they should also contribute to better understanding of the extent of risk to the wildlife health associated with chronic exposure to mercury.

4a: Informing the implementation of the Minamata Convention: the role of scientific assessments

TP-171

BIOLOGICAL MERCURY HOTSPOTS IN THE WATERSHEDS OF THE MESOAMERICAN BARRIER REEF SYSTEM

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The Mesoamerican Barrier Reef System (MBRS) is the largest barrier reef in the Northern Hemisphere, extending over 1000 kilometers from the Yucatan Peninsula of Mexico to the Bay Islands of northern Honduras. It is a UNESCO World Heritage Site, renowned for its marine biodiversity. An estimated 2 million people from Mexico, Belize, Guatemala, and Honduras depend on the reef for their economic livelihoods.

A series of stressors are impacting the health of the reef including rapid coastal development, overfishing, and poor agricultural practices within the watersheds that drain into the reef. In addition, recent data suggest that mercury contamination may be impacting both freshwater and marine fishes of the barrier reef ecosystem. Here, we present mercury concentrations from more than 700 individual fishes including both freshwater and marine species. Freshwater fishes were collected in the major watersheds of Belize, Guatemala, and Honduras that drain into the barrier reef. Additional marine species were collected via market landings and direct capture.

Results highlight biological mercury hotspots where fish mercury concentrations are elevated above both U.S. EPA and World Health Organization human consumption guidelines. Hotspots include the Chalillo Reservoir and upper Belize River in Belize and Lago Yojoa of northern Honduras. In addition, we identify freshwater and marine species that represent both healthy and risky choices for human fish consumption. Riskier choices include amberjack, mackerel and barracuda with average mercury concentrations above 0.5 parts per million, wet weight (ppm, ww). Healthier choices are fishes with mercury concentrations below 0.3 ppm (ww) and include hogfish, spiny lobster, and several species of snapper. These data provide a potential model for future human health consumption guidelines for freshwater and marine fishes of the MBRS and also the need for more extensive research on potential sources of contaminants in the greater MBRS watershed.

TP-172

FULFILLING OBLIGATIONS OF THE MINAMATA CONVENTION ON MERCURY FOR NATIONS: MINAMATA INITIAL ASSESSMENTS

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In response to growing international concern about mercury pollution, the United Nations Environment Programme (UNEP) formalized the Global Mercury Partnership in 2008 to systematically eliminate anthropogenic mercury releases through strategic intervention and collaboration with national governments. As of 2009, UNEPs governing council entered negotiations for the preparation of a legally binding global instrument on mercury to safeguard human and ecosystem health. Negotiations were successfully completed in January 2013 with 147 governments agreeing on draft text. At the Conference of Plenipotentiaries on 9-11 October, 2013 in Minamata and Kumamoto, Japan, the Minamata Convention on Mercury was formally adopted and opened for signature.

The Minamata Convention has a phased approach to reduce, and where possible, eliminate mercury use in key industrial sectors. Provisions of the Convention include phase out deadlines established for supply sources and trade, mercury added products, and manufacturing processes in which mercury or mercury compounds are used. Based on these targets, the Convention is designed to systematically reduce emissions and releases to land and water, and phase out the use of mercury where alternatives exist.

To meet obligations under the Convention, several barriers must be addressed to assist in ratification. These barriers include: (1) lack of institutional capacity to implement the Convention; (2) gaps in political and legislative frameworks to support Convention provisions; (3) lack of data on sources of emissions and releases, as well as outdated national inventories of mercury stocks; and (4) low awareness of health risks associated with mercury among the public and government officials. With the adoption of the Convention, countries generally require assistance to formulate and apply sector wide programs.

The development of the Minamata Initial Assessment (MIA) addresses these barriers by providing standardized, basic and essential information to enable policy and strategic decisions to be made and assist in developing plans to identify priority sectors and activities within the country and to increase awareness of risks to human and ecosystem health. The use of financial support from the Global Environment Facility (GEF) enables nations to fulfill essential communication requirements, make informed policy decisions and assist in prioritizing activities. Over 90 countries are now conducting MIAs through GEF funding.

Biodiversity Research Institute (BRI) is an executing agency for the United Nations Environment Programme, United Nations Industrial Development Organization (UNIDO) and the United Nations Development Programme (UNDP). BRI is conducting and is now involved with MIAs in over 30 countries.

TP-173

THE ROLE THAT THE CANADIAN MERCURY SCIENCE ASSESSMENT CAN PLAY TO INFORM GOVERNMENTS PLANNING THE IMPLEMENTATION OF THE MINAMATA CONVENTION

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Scientific assessments are good tools used to synthesize extensive information into relevant and useful summaries on a topical issue. Generally, science assessments evaluate the past and current scientific status of an issue; identify priorities for future scientific needs and inform the scientific community on the state of research. In addition, they provide evidence for decision-making by research managers and policy-makers on scientific issues. The Canadian Mercury Science Assessment (CMSA) is the first nationally comprehensive, peer-reviewed synthesis of scientific knowledge on mercury in Canada and was released in 2016/17. This report was intended to provide information to support Canadas domestic policy and science priorities as well as provide a scientific foundation, from the Canadian perspective, for the development of efforts to reduce global mercury emissions in the implementation of the Minamata Convention.

Preparation of this assessment began with a series of workshops where science questions were developed to capture the information needs of the science and policy communities in Canada. Based on these questions, the goal of this assessment was to respond to the questions through a synthesis of knowledge on environmental mercury pollution.

Results from Canadas Mercury Science Program (part of Canadas then Clean Air Regulatory Agenda) were used as a platform for the assessment as well as other mercury research programs. Researchers were tasked with quantifying current and past levels of mercury in the environment, identifying gaps in our knowledge of the transport routes from point of emission to exposure to wildlife and humans. Further, researchers were challenged to develop the capacity to predict changes in indicators associated with changes in levels of emissions of mercury or changes in the receiving environment. This information was combined in a full 15 chapter assessment report.

The CMSA consists of 3 documents: the Executive, Summary the Summary of Key Results and the full Science Assessment. The Executive Summary is a short document highlighting the high level results. The Summary of Key Results contains the answers to the policy-relevant science questions. The full Science Assessment provides an in-depth knowledge on mercury levels and processes in the Canadian environment and identifies gaps in our understanding of how mercury travels though the ecosystem, where it ends up, the impact of human activities on its chemistry and changes in mercury pollution.

A full summary of the CMSA and its impact on informing decision-makers for the Minamata Convention will be discussed.

TP-174

AN ASSESSMENT OF MERCURY CONTAMINATED SITES IN LOW AND MIDDLE INCOME COUNTRIES

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Pure Earths (PE) Toxic Site Identification Program (TSIP) works globally to identify and assess polluted sites that pose a risk to public health. Though not comprehensive, TSIP works to improve public health in low- and middle-income countries (LMICs) while being culturally and socially considerate and responsible.

Mercury (Hg) is a naturally occurring metal found in air, water and soil. Because of its damaging effects to public health and persistence as a global toxicant, the WHO placed mercury on its top ten list of chemicals of major public health concern. Despite being highly toxic, even in small amounts, it is used, unshielded, and released in several LMICs during the extraction of gold and ore processing.

In November 2016, data for 463 mercury-contaminated sites in LMICs were extracted from the TSIP database to review descriptive statistics where mercury (elemental, inorganic or organic) is identified as the key pollutant.

The TSIP database query notes distribution of mercury as a key pollutant as follows: 168 in Africa (36.3%), 97 in Central and South America (20.9%), 12 in China (2.6%), 37 in Eastern Europe (8.0%), 26 in South Asia (5.6%), and 123 in Southeast Asia (26.6%). 154 sites (33.3%) have verified health effects. The average population potentially at risk of mercury exposure at each site is approximately18,000. Artisanal Mining (Hand Mining), the largest industry contributing to global mercury emissions, represents nearly half (49.46%, 229 sites) of the TSIP sites with mercury as a key pollutant, distantly followed by formal Mining and Ore Processing (21.38%, 99 sites).

These results give insight into the effects of mercury and its global prevalence and detriment. The results are used by PE to prioritize limited funding to conduct additional assessment and to support cleanup at sites that have the highest risk.

TP-175

THE ROLES OF THE HEALTH SECTOR IN THE MINAMATA CONVENTION IMPLEMENTATION: RAISING AWARENESS AND STRENGTHENING CAPABILITIES

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In support of the Minamata Convention, the World Health Organization adopted the World Health Assembly Resolution 67.11: Public health impacts of exposure to mercury and mercury compounds: the role of WHO and ministries of public health in the implementation of the Minamata Convention. These roles are well defined and evolved from the United Nations Environment Program and International Negotiating Committee meetings, held during 2009 and 2016, in which WHO participated.

The Convention urges member states to act on the development and implementation of strategies and programs to identify and protect population at risk, particularly vulnerable populations, from exposure to mercury and mercury compounds. Recommendations include setting targets for mercury exposure reduction, and public education and awareness. In this regard, phase-out of mercury-added products in medical devices (i.e. thermometers and sphygmomanometers) and in products (i.e. antiseptics and skin-lightening cosmetics) is among the health sector responsibilities. In addition, dental amalgam use is under phase-down, for which additional resources are needed for its effective use reduction. For instance, the effective switch to non-amalgam materials should count with health insurance companies to incorporate reimbursement mechanisms; therefore providing higher economic support to persons using non-amalgam material.

Considering the significance of atmospheric mercury emission from the artisanal and small scale gold mining (ASGM) sector, the development of national action plans to eliminate or reduce mercury use is needed, especially for countries that declare ASGM as significant. Noting that public health strategies are required for ASGM national action plans, WHO/PAHO has been developing guideline documents to address development and implementation of such strategies.

Fish consumption is also a relevant aspect of the Convention, given the nutritional benefits and mercury risks involved, especially among women of reproductive age. Heavy fish-eating communities living in areas under the influence of ASGM have been considered the most vulnerable populations for methyl mercury exposure. Opportunities to further develop fish advisories, ideally based on local biomonitoring data, are warranted. - Dissemination of WHO guidelines, health sector capacity building, and coordination of information exchanges have been addressed in regional workshops conducted in Uruguay and Jamaica by WHO/PAHO, and Germany and Jordan, by respective regional offices for health representatives. To strengthen health sector capabilities, these topics above mentioned are addressed in the PAHO Virtual Campus course on mercury.

TP-176

EVALUATING REPRODUCIBILITY OF MERCURY SCIENCE, MODELS AND BIOMONITORING: IMPLICATIONS FOR THE MINAMATA CONVENTION

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Reproducibility is a cornerstone of the scientific method and, in principle, is an essential part of the scientific process. In recent years mercury science has evolved significantly with its use of advanced technologies and computational models to address this complex environmental and public health issue. These advances in the field have made it essential that transparency be enhanced to ensure that mercury studies are truly reproducible and scientifically sound. The goal of this presentation is to evaluate methods, results and inferential reproducibility as it relates to uncertainty in mercury research models, science, and biomonitoring. Here I use peer reviewed, published studies to evaluate reproducibility in several key mercury investigations especially with regard to how it relates to policymaking. I will provide examples of the overall principle of reproducibility and discuss the role of transparency, peer review, basic reporting and open data access standards. Lastly, I will also present a framework to reduce irreproducibility in mercury research studies, models and biomonitoring investigations in support of the Minamata Convention on Mercury.

TP-177

USING SEABIRDS AS BIOMONITORS OF TEMPORAL AND SPATIAL TRENDS OF MERCURY FOR THE MINAMATA CONVENTION

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Marine ecosystems are impacted at the global scale by Hg and the combined effects of climate change and human activities could lead to a dramatic increase of its bioaccumulation in marine organisms in the future. Indeed, the general warming of ocean water masses is affecting the cycle of Hg (e.g., its methylation rate), thereby increasing exposure of marine organisms. In that context, providing a large-scale and comprehensive understanding of marine food web contamination is essential to better comprehend the impacts of anthropogenic activities and climate change on bioaccumulation of Hg in marine organisms and to propose mitigation measures in the frame of the Minamata Convention. Monitoring at large scales, both spatially and temporally, are relevant to such evaluation. In this way, we propose to use seabirds as bioindicators of the environmental global contamination by Hg. Seabirds are indeed relevant organisms to monitor Hg as: 1) they are excellent indicators of Hg contamination and reflect the contamination of the entire food chain on which they rely; 2) they have a wide distribution and different species occupy various compartments of their ecosystems (inshore or offshore, benthic or surface feeders, piscivorous or zooplankton-feeders); 3) most species are colonial and philopatric, giving the opportunity to sample several individuals simultaneously and to monitor them repeatedly through time since non-lethal sampling of blood (short-time exposure) and feathers (long-term exposure) is easy in seabirds; 4) feathers can be collected from Museum specimens, allowing retrospective investigation of Hg time trends. Seabirds therefore appear to be ideal organisms to (1) monitor spatial variations of Hg in marine ecosystems at different latitudes (2) define hotspots of Hg contamination in the different large ecosystems and highlight sensitive areas that require particular attention and protection (3) carry long-term monitoring of Hg trends in the different parts of the world Ocean. An effort is now needed to generate an integrated and standardized biomonitoring network to determine spatial and temporal trends of Hg to help evaluate the effectiveness of the Minamata Convention.

4b: Contaminated site assessment and management: Lessons for technical assistance under the Minamata Convention

TP-178

MOBILITY OF MERCURY INSIDE TWO LANDFILL SITES IN JAPAN

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Landfills have been identified as vital source of mercury (Hg) emissions to the environment. Although there are some reports available for understanding influence of landfill site on environmental mercury pollution, only a few studies were carried out for assessment of mobility of mercury inside landfill site, which might be significant for environmental sound management of mercury waste. Therefore in the present study, core samplings in two landfills were conducted to evaluate stability of mercury in waste and gaseous phase Hg speciation was examined using Ontario Hydro (OH) Method with the aim of distinguishing elemental Hg and oxidized Hg in landfill gas (LFG). Leachate from two landfills was also collected seasonally. Total Hg (T-Hg) concentration in Landfill A ranged from 4 to 1910 μg kg-1 with a geometric mean of 292 μg kg-1 (n=29), meanwhile, T-Hg concentration in Landfill B ranged from 3 to 1368 μg kg-1 with a geometric mean of 556 μg kg-1 (n=35). Generally, T-Hg of Landfill B was higher than that of Landfill A, which is possibly because incineration fly ash which contained more Hg were accepted. Results of Japanese leaching test (JLT-13) which was applied to evaluate the Hg mobility from solid phase to liquid phase were under the detection limit and might indicate Hg was still stabilized in solid phase. The gaseous Hg in LFG was in the μg m-3 range of two landfills, which was similar to previous reports of gaseous Hg emission from landfills (e.g. the Florida case and the Seoul case). The ratio of oxidized Hg varied a lot ranged from 40% to 60% while literatures reported methylated compounds occupied about 10% in the US landfills, which might because ionic Hg was also absorbed as oxidized speciation in OH Method. In the case of leachate, T-Hg was slightly detected in Landfill A at the range of 0.1 μg L-1, on the country, no detection from Landfill B, which coincided with the results of JLT-13. Hg in the solid phase was highly detected as other studies and Hg disposed in landfills usually caused concern about its mobility to natural environment. Nevertheless, the low level results of leaching test and leachate collected on site corroborated the safety of the two landfills. Compared with leachate, LFG seemed to be a predominant release pathway of Hg. All these results indicated the vast majority of Hg remained in the solid phase and was stabilized to some extent.

TP-179

GAPS ANALYSIS OF IMPLEMENTING MINAMATA CONVENTION IN TWO TYPICAL HG-CONTAMINATED SITES IN CHINA

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At present, due to the rapid development of industry, a large quantity of mercury (Hg) contaminated sites distributed worldwide. Simultaneously, being a global pollutant, mercury is characterized with a persistence, high bio-accumulation, eco-toxicity, and long-distance transport. Mercury pollutants not only can cause risk to environment and human health, but also hamper further economy development. According to the aim of sub-project on Chinese Hg-contaminated sites in SINOMER Phase □, two typical Hg-contaminated sites of mercury mining areas and mercury cell chlor-alkali processing plants were selected to generalize a preliminary reports on gaps analysis for sites information, remediation techniques, policies, management, and public awareness in China.

Gaps for China Hg-contaminated sites implementing for Minamata Convention exist in the following aspects: 1) Information gaps: a national list of Hg-contaminated sites has not been established in China, mercury levels in environmental compartments as well as actions of remediation are lack, and information of some recorded sites are incomplete; 2) Policy gaps: the current laws and regulations related to Hg-contaminated sites are not comprehensive, laws or regulations specifically aimed at Hg-contaminated sites have not been established. A further improvement of both national technical guidelines and guides, and environmental standards contaminated sites related are necessary. Furthermore, the regional variation and land use related to contaminated sites also need to investigate; 3) Technique gaps: a series of technical specifications for environmental monitoring have introduced, a series of technical guides and rules for contaminated sites risk assessment were recently introduced. Contaminated sites monitoring technologies were preliminary established. The adopted remediation techniques of mercury pollution are limited. The phytoremediation, weir deposition, and other technologies are needed to carry out; 4) Management gaps: the environmental sound management of contaminated sites is still in the initial stage. The environmental sound management system focusing on eco risks assessment has not been established. The special regulatory agencies and personnels are required; 5): Awareness gaps: the existing information of Hg-contaminated sites has not been shared. The populations are lack of the knowledge on Hg characteristics, toxicity, and protection. And also Hg toxicity protection on public institution and activities are scare.

TP-180

EFFECT OF FLOW RATE AND TEMPERATURE ON MERCURY DESORPTION KINETICS DURING IN SITU THERMAL DESORPTION

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Mercury is listed by the USEPA as among the most toxic chemicals on earth due to its natural occurrence and persistence in the environment, and its highly toxic nature. The toxicity of mercury became apparent after the Minamata disease which first occurred in the 1950s. Still, there are many recent and ongoing researches investigating other pathways of mercury to the human system and the diseases it brings about. Various studies around the world investigated and described mercury accumulation in soils, plants, bodies of water, and fish species in various locations around the world. With the variation of soil types and contamination sources, several characterization and speciation methods were also designed, implemented and investigated for adequacy and efficiency. Thermal treatment has already been in use as a remediation method for soil contaminated by heavy metals even before its application to the characterization of mercury in soil. More recent

studies have analyzed and proven its potential and validity to remediate mercury contaminated soils. Thermal desorption studies show that in comparison to desorption time, temperature has a greater effect on the mercury removal rate. These studies, however, gave different values of temperature (100°C and 400°C) at which mercury removal becomes very efficient. This difference can be justified by the variations in the mercury species and their corresponding concentrations in the soil samples studied. It may then be necessary to further study at which temperatures each mercury species get to be removed from the soil. Quartz columns are filled with mercury contaminated soil and are secured using glass wool. Heat is applied to the column while N2 gas carries mercury species into the cold vapor atomic fluorescence spectrometry (CVAFS) detector. SnCl2 reduction, purge and trap gold amalgamation pre-concentration, and cold vapor atomic fluorescence spectrometry (CVAFS) detection as per US EPA Method 1631 were implemented for standardization. Experimental results show that at low temperatures (<200°C), HgCl2 desorption amount is higher than HgO, HgS. At temperatures equal to or greater than 300°C, about 97 to 99% of HgO, HgS and HgCl2 contaminated soils are removed from the sample within a span of six hours, respectively. The effect of varying temperatures applied and air flow rates to the thermal desorption kinetics were studied.

TP-181

MAPPING GASEOUS MERCURY CONCENTRATIONS AROUND AN ABANDONED MINE IN ITALY USING PASSIVE AIR SAMPLERS

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The Abbadia San Salvatore mercury (Hg) mine was the largest mine of the Mount Amiata Hg ore district (Central Italy) and the third largest site of Hg production during the 20th Century. Despite the cessation of operations in 1983 and recent remediation work, the mine remains a major source of Hg to the environment, especially the atmosphere. To map the atmospheric dispersion of gaseous Hg in the region we employed our recently calibrated passive air sampler for gaseous Hg. Sampling was conducted across two 7-by-7 sampling grids: at a fine-spatial scale (~1 km2 total area) around the mine itself (week long deployments in October 2015 and July 2016) and in a coarser grid (~50 km2 total area) across the western slope of Mt. Amiata (four 3-month deployments in 2015/16). This constitutes the first highly spatially resolved mapping of concurrent, time-averaged gaseous Hg concentrations in and around a major Hg source. Concentrations are in good agreement with instantaneous, but non-concurrent measurements previously reported for the mine site. In the mine area concentrations reach as high as 12,500 ng m-3 and decline rapidly with distance from the most contaminated site. In July, concentrations are higher than in October, especially around the central, most contaminated sites and sites downwind (to the east). This causes concentrations in the closest residential areas of the town of Abbadia San Salvatore to reach or even exceed chronic exposure guideline levels (200 ng m-3). Seasonal deployments across the larger Mt Amiata region also show elevated concentrations in the summer closer to the mine, presumably because emissions increase with temperature. Further from the mine concentrations are remarkably consistent between seasons and show a concentric pattern of rapid decline with distance from the mine, which is skewed to the east by the dominant westerly winds. Background concentrations are observed at sites furthest to the west of the mine. The incremental increase in concentrations moving from upwind background sites towards the mine demonstrates the capability of the sampler to resolve fine differences at background concentrations with a high level of precision and accuracy (<0.2 ng m-3).

4c: Anthropogenic emissions: Monitoring and analysis to support mitigation

TP-182

USING PASSIVE AIR SAMPLERS TO MAP GASEOUS MERCURY CONCENTRATIONS ACROSS AN URBAN ENVIRONMENT: GREATER TORONTO AREA

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Atmospheric mercury (Hg) has both natural and anthropogenic sources. The latter include artisanal gold mining, coal combustion, chlor-alkali industry, production of cement and certain metals, crematoria, waste disposal and recycling (especially Hg containing products), and production of Hg containing devices (batteries, fluorescent light bulbs). While many urban sources have been remediated or relocated outside of cities in developed countries, legacy sources may remain and poorly identified, continuing sources may exist. We deployed our recently developed passive air sampler for gaseous Hg at a total of 161 sites across the Greater Toronto Area (GTA), with a greater density of sampling sites in the City of Toronto itself. Prior to sampling, we identified likely source locations grouped as either waste disposal and recycling facilities, crematoria, or hospitals and dental clinics. The deployment included 103 additional sites at the homes of graduate students, staff, and faculty of the University of Toronto Scarborough, and other locations where the relative spatial density of deployments was low. Additionally, a downwind transect of samplers was deployed at a regional Hg disposal and recovery facility located near Kitchener, Ontario. Mean gaseous Hg concentration near waste disposal and recycling facilities (1.9 ± 0.3 ng m-3), crematoria (1.8 ± 0.2 ng m-3), and hospitals and dental clinics (1.9 ± 0.3 ng m-3) sites are all slightly, but significantly ($p < 0.05$), higher than at the remaining sites (1.6 ± 0.2 ng m-3). The three potential source groupings are not significantly different from each other ($p > 0.05$). Geospatial interpolation of the data reveals slightly elevated concentrations in the central business district of the City of Toronto, an area that also includes six hospitals, and a general decline of gaseous mercury concentrations toward the eastern Greater Toronto Area. Gaseous Hg concentrations decrease along a transect of increasing distance from the Hg disposal and recovery facility near Kitchener, ranging from 13.7 (~10 m SW of the central building) to 1.5 ng m-3 (2.2 km SSE of the site). This study demonstrates that passive sampling using this method can be sufficiently precise to spatially distinguish small (<0.2 ng m-3) gaseous Hg concentration differences at and around global background levels. Furthermore, the sampler can be used as a valuable tool for identifying point sources in urban areas that may previously have been described as diffuse source regions.

TP-183

IMPACTS FROM LOCAL SOURCES COMPARED TO LONG-RANGE TRANSPORT OF TOTAL GASEOUS MERCURY (TGM) CONCENTRATIONS IN INDUSTRIAL COMPLEXES IN SOUTH KOREA

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The objectives of this study were to: (1) characterize the hourly and seasonal variations of atmospheric total gaseous mercury (TGM) concentrations, (2) identify the relationships between TGM and co-pollutants concentrations, (3) characterize high TGM concentration events by distinguishing between long-range transport events and local events, and (4) identify likely source directions and locations of TGM using conditional probability function (CPF), conditional bivariate probability function (CBPF) and potential source contribution function (PSCF) for Gwangyang City, Jeollanam-do, a province in southern South Korea. Gwangyang City is heavily industrialized with large steel manufacturing facility and there are iron and steel manufacturing facilities including electric and sintering furnaces using coking around the sampling site. In addition, there is Yeosu City which includes a large petrochemical complex from the west of the sampling site.

TGM concentrations were measured every 5 min during spring (11 May-6 June 2016), and fall (2-10 November 2016) on the roof of the public bath house using a Tekran 2537B. Hourly meteorological data and concentrations of SO2, NO2, O3, CO, PM10 and PM2.5 were obtained from the Korea Meteorological Administration (KMA) and the National Air Quality Monitoring Network (NAQMN), respectively.

The TGM concentration was statistically significantly higher in fall (1.4 ± 1.2 ng m-3) than in spring (0.8 ± 0.6 ng m-3) ($p<0.01$). The TGM concentrations in spring were simultaneously positively correlated with SO2 ($r = 0.31$, $p<0.01$), NO2 ($r = 0.22$, $p<0.01$), PM10 ($r = 0.31$, $p<0.01$) and PM2.5 ($r = 0.23$, $p<0.01$). Compared to spring, the TGM concentrations in fall have strong positive correlation with CO ($r = 0.94$, $p<0.01$), NO2 ($r = 0.53$, $p<0.01$), PM10 ($r = 0.71$, $p<0.01$) and PM2.5 ($r = 0.26$, $p<0.01$) due to an extreme pollution episode with very high TGM concentrations.

A total of 3 high TGM concentration events were identified based on ΔTGM/ΔCO slopes and correlations between TGM and CO concentrations; 2 long-range transport events and 1 local event. Backward trajectory analysis showed that air parcels arrived from China during long-range transport events.

CPF, CBPF and PSCF plots indicated that the main sources of TGM were west of the sample site and included iron and steel manufacturing facilities and the east of the site including cement production facilities. Southeast of the sampling site was also identified as a likely source area of TGM where Yeosu City, the location of a large petrochemical complex and known TGM source.

TP-184

MIGRATION AND TRANSPORT OF ATMOSPHERIC MERCURY FROM A MINING REGION OF QUERÉTARO (SAN JOAQUÍN) AND ITS IMPACT ON THE CITY OF QUERÉTARO, MÉXICO

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The study of mercury (Hg) in its different chemical forms in the environment has developed greatly in the US, Canada, Japan and other countries. However in Mxico, few studies have been performed in urban, rural coastal and mining areas. The objective of this study was to evaluate the concentration of mercury (Hg) in particulate matter (PM10) in a mining zone the 2014 to 2015 years. Therefore, the people who live around this mining region are the most affected because they are exposed to the mercury in a chronicle way which is also in high concentrations. Chronic exposure to this metal can get to affect human health causing severe damage to the immune system. Estimating the atmospheric concentrations of PM10-bounded Hg in mining areas is crucial for evaluating adverse health impacts. In the current study, a combination of measurements and multivariate statistical tools was used to investigate the influence of mines activities on variations in the concentrations of particulate mercury (HgP) in ambient air. San Joaqun is a mining region south of the Sierra Gorda of Queretaro, Mexico. The concentrations of Hg in PM10 were measured simultaneously at two air sites. The comparatively low coefficients of divergence (COD) that were found in the majority of samples highlight that site-specific effects are of minor importance. A principal component analysis (PCA) revealed that 37.74 %, 13.51 %, and 11.32 % of the total variances represent mines emissions, vehicular exhausts. This analysis allows determining the extent of contamination by mercury within each environmental component, as well as the detection of its maximum and minimum thresholds. For a better understanding of mercury distribution in each component, box and whiskers diagrams were used through STATISTICA Version 10 software. Emphasis is given to the associations between Hg concentrations and local meteorological conditions.

TP-185

IDENTIFICATION AND CHARACTERIZATION OF A POTENTIAL CREMATORIUM MERCURY EMISSION SOURCE

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Mercury is a global pollutant with serious harmful impacts on human and ecosystem health. It is emitted into the atmosphere from many sources such as fossil fuel combustion, incineration, and landfill. Some sources/processes are either poorly documented or unknown. Cremation processes are one of these that have not been studied and are currently unaccounted for in the United States Environmental Protection Agency's National Emissions Inventory. The objective of this study was to characterize the temporal variation of total gaseous mercury (TGM) concentrations and identify an unknown, seemingly highly localized source of gaseous mercury causing very high episodic concentrations. TGM measurements were conducted from the State University of New York College of Environmental Science and Forestry (SUNY-ESF) campus in downtown Syracuse, New York during the time period of summer 2013 – fall 2015. A complete annual cycle was observed, with lowest concentrations (1.36 ng m^{-3}) in September, and highest (1.57 ng m^{-3}) in January, with an annual average amplitude of 0.21 ng m^{-3}. Concentrations appeared to be decreasing continuously throughout the study period, with decreases of 0.12 ng m^{-3} and 0.18 ng m^{-3} for summer 2013-2014 and 2014-2015, respectively; 0.14 ng m^{-3} and 0.05 ng m^{-3} for fall 2013-2014 and 2014-2015, respectively; and 0.08 ng m^{-3} for winter 2014-2015. Diurnal cycles were observed with daily maximums at 13:00-16:00 UTC (1.55 ng m^{-3} - 1.65 ng m^{-3}) in winter-spring, 1:00 UTC (1.4 ng m^{-3} – 1.7 ng m^{-3}) and 12:00-16:00 UTC (1.3 ng m^{-3} – 1.52 ng m^{-3}) in summer-fall. The concentrations above the seasonal 99th percentile values under calm (< 2 m s^{-1}) and southeasterly wind conditions were associated with probable Hg emissions from a nearby crematorium, located approximately 890 meters to the southeast of the monitoring station. The total emission of mercury from this source was estimated to be 0.51 lbs, 1.64 lbs, and 0.49 lbs for 2013, 2014, and 2015, respectively. These were compared to nearby sources documented in the EPA's National Emissions Inventory 2011, including the Syracuse Steam Station (0.3 lbs), Onondaga County Resource Recovery Facility (7.7 lbs) and Bristol-Myer Squibb Company (9.52E-02 lbs). Further study is warranted to determine the extent of mercury emissions from crematoriums across the United States.

TP-186

EFFECT OF PROCESS CONDITIONS ON MERCURY EMISSIONS FROM A FLUIDIZED BED SEWAGE SLUDGE INCINERATOR

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Wastewater entering municipal wastewater treatment plants (WWTPs) contains mercury (Hg) from domestic, commercial, and industrial sources. During treatment, almost all of that Hg (>98%) ends up in the sludge residual stream, and Hg concentrations in the treated wastewater effluent are typically quite low (<10 ng/L). Many larger WWTPs in metropolitan areas incinerate their sludge onsite. U.S. Environmental Protection Agency (EPA) regulations for existing fluidized bed reactor (FBR) sewage sludge incinerators limit Hg concentrations in the stack emissions to 37,000 ng/DSCM (at 7% O2). The limit for new fluidized bed reactors (FBRs built after October 14, 2010) is much lower (1000 ng/DSCM). At the Metropolitan Wastewater Treatment Plant (St. Paul, Minnesota, USA), dewatered primary and waste secondary sludge is incinerated in three FBRs at a rate of approximately 230 dry tons/day. The process trains for each FBR include energy recovery and air pollution control (APC) equipment, including activated carbon addition to the exhaust gas stream for Hg control, and baghouses for combustion ash and carbon removal. Here, we use EPA Method 30B to measure the in-stack Hg concentrations for one of these FBRs, and attempt to correlate Hg emission levels with particular process operating parameters. The results show that the APC equipment is capable of removing Hg to very low levels. Actual measured Hg concentrations in the stack gas ranged from 11 to 300 ng/DSCM (at 7% O2), increasing with higher dust levels in the baghouse outlet stream, and decreasing with increasing carbon feed rate. Actual Hg mass emission rates ranged from 0.01 to 0.25 g/day for this particular FBR.

TP-187

USE OF A QUADCOPTER FOR TARGETED SAMPLING OF GASEOUS MERCURY IN THE ATMOSPHERE

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Because mercury (Hg) is a toxic global pollutant dispersed through the atmosphere, measuring it is important to apportion sources and determine spatial and temporal trends in deposition and air concentrations. Here, we modified a popular and inexpensive quadcopter to collect gaseous mercury (Hg) on gold-coated quartz cartridges. The gold traps were analyzed in the laboratory using cold vapor atomic fluorescence spectrometry (USEPA Method IO-5). The purpose was to determine the feasibility of using the method to measure ambient Hg concentrations at precise locations aloft and to detect emissions from a known point source. To that end, the quadcopter was outfitted with a pump, three gold coated quartz cartridges, one colorimetric SO2 (Drager) tube, and syringe filters (0.2 µm, PTFE). Flight times averaged 15 minutes, limited by battery life, and yielded >5 pg of Hg, well above the <0.1 pg detection limit. Method precision averaged 12% RSD (range 4.3% to 28%). Demonstrating that the technique can measure elevated emissions of Hg from a point source, we measured progressively higher concentrations nearer a pool of elemental Hg placed atop a ladder in an open field. We applied the method near two coal fired power plants (CFPPs) and a petroleum refinery in the mid-south USA. Concentrations (mean ± SD) near the rural Red Hills Power Plant were 1.5 ± 0.2 ng m-3 downwind and 1.3 ± 0.1 ng m-3 upwind. Concentrations near the Allen Fossil Plant were 1.9 ± 0.1 ng m-3 downwind and 2.0 ± 0.1 ng m-3 upwind. However, because of distance from the stacks (dilution) we do not know if sampling occurred in the actual power plant plumes, and these concentrations likely reflect ambient air rather than the near-field plume. Concentrations near the refinery were also similar downwind and upwind (3.2 ± 0.6 ng m-3 and 3.3 ± 0.9 ng m-3, respectively), but elevated compared to the rural location. Overall, this study demonstrates that highly maneuverable multicopters can be used to probe Hg concentrations aloft. Because of portability, the method may be particularly useful for evaluating Hg emissions from landscapes and transient sources, such as biomass burning, which are poorly characterized and leading to uncertainties in ecosystem budgets. However, before using multicopters for air sampling, air space and flight restrictions must be carefully considered.

TP-189

THE IMPACT OF LOCAL URBAN SOURCES ON TOTAL ATMOSPHERIC MERCURY WET DEPOSITION IN CLEVELAND, OHIO, USA

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Event-based precipitation samples were collected at a downtown industrial and a predominantly upwind rural location in the Cleveland, Ohio metropolitan area from July 2009 through December 2010 to investigate the potential local total mercury (Hg) wet deposition enhancement in a region with a high concentration of coal combustion sources. Total Hg wet deposition for the 18-month period was 6.8 µg/m2 (n = 81) at the rural site and 10.7 µg/m2 (n = 98) at the urban site demonstrating a significant (p = 0.046) 37% enhancement in deposition between the two sites. Large deposition events (>0.2 µg/m2) occurred predominantly from May through October [n = 16 (urban), n = 10 (rural)] and represented from 2 to 8% of total 18-month deposition per event. At the downtown urban site, the average Hg precipitation concentration was 53% higher for these large deposition events. Concurrently measured precipitation events delivered in aggregate 2.4 times more total Hg wet deposition to the urban site compared to the rural site. Hg rainfall concentrations for concurrent events with similar precipitation depth were 2-4 times higher at the urban site and suggest scavenging of local Hg emissions. Further evaluation of these events revealed 83% more total Hg deposition at the urban site from January to December 2010 compared to July to December 2009, while there was 26% more at the rural site during these same time periods. The larger increase in deposition at the urban site in 2010 may be evidence of increased local emissions from sources that were known to be offline during this study period because of an economic recession.

TP-190

A STUDY ON THE MERCURY CONTINUOUS EMISSION MONITORING AND SPECIATION FOR MEDICAL WASTE INCINERATOR

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In recent years, national attention has been given to the emission characteristics of mercury compounds and their behavior in the air. Therefore, it is necessary to conduct a national-level research about the inventory of domestic mercury compound emission sources and to develop distribution factors to calculate the emission quantity. This study had three objectives: (1) process for conducting a relative accuracy test audit of Continuous Emission Monitor; (2) study mercury behavior in incineration sources; (3) evaluate the influence of emission sources on ambient point. To understand mercury behavior at medical waste incinerator (MWI), their concentrations at the stack were monitored continuously for three month. During the same period we conducted a relative accuracy test audit of Mercury Continuous Emission Monitor (Hg CEM) using Ontario-Hydro Method and Method 30B. The relative accuracy of Hg CEM with respect to Ontario-Hydro Method and Method 30B as reference method result was 9.38 % and 7.38 % (20.00 % limit). As such, the Hg CEM data passed the RATA. Mercury concentration in flue gas of MWI was 1.05 ~ 280 ug/Sm3, and many cases of short term high concentration occurred. Mercury speciation testing using mercury CEM and Ontario-Hydro Method of showed 26 % elemental Hg, 74 % oxidized Hg in stack. To figure out how mercury affects ambient site from the emission source, we selected ambient site using Industrial Source Complex Short Term 3 and measured mercury continuously for a month and compared evaluation with equipped CEM at MWI. Mercury concentration of ambient site shows mostly clean level (0.90 ~ 2.99 ng/Sm3), but in the monitoring period, the episode was occurred twice that considered to have an affected from the emission source. Further studies on the effects of emission sources on the ambient site will be needed in the future.

TP-193

IDENTIFICATIONS OF LOCAL SOURCES OF TOTAL GASEOUS MERCURY (TGM) CONCENTRATIONS IN INDUSTRIAL COMPLEXES IN SOUTH KOREA

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The objectives of this study were to: (1) characterize the diurnal and seasonal variations of atmospheric total gaseous mercury (TGM) concentrations, (2) investigate the relationships between TGM and co-pollutants concentrations, and (3) identify likely source directions and locations of TGM using conditional probability function (CPF), conditional bivariate probability function (CBPF) and potential source contribution function (PSCF) for Ansan City, South Korea. There are two national industrial complexes (Sihwa and Banwol) which consist of the manufacturing, electronics industries, the petroleum refineries and the steel industry around the sampling site.

TGM concentrations were measured every 5 min during spring (11-19 May 2015), summer (28 July-04 August 2015), and fall (13-21 October 2015) on the roof of the Choji high school using a Tekran 2537B. Hourly meteorological data and concentrations of NO2, O3, CO, PM10 and SO2 were obtained from the Korea Meteorological Administration (KMA) and the National Air Quality Monitoring Network (NAQMN), respectively.

The TGM concentration was statistically significantly higher in spring (2.7 ± .0 ng m-3) than other seasons (p<0.01), followed by fall (2.5 ± 0.8 ng m-3) and summer (1.9 ± 0.5 ng m-3).The TGM concentrations generally showed a consistent increase around 7:00 due to local emissions related to increased traffic, industrial activities, and activation of local surface emission sources.

The TGM concentrations were simultaneously positively correlated with CO (r = 0.42, p<0.01), NO2 (r = 0.39, p<0.01) and PM10 (r = 0.51, p<0.01), suggesting that combustion processes are an important source.

There was a significantly positive correlation between TGM and CO in this study (r = 0.42, p<0.01), suggesting that TGM and CO were affected by similar anthropogenic emission sources. However, the observed ΔTGM/ΔCO was 0.0031 ng m-3 ppbv-1 in spring, 0.0026 ng m-3 ppbv-1 in summer, 0.0030 ng m-3 ppbv-1 in fall, which are significantly lower than that indicative of Asian long-range transport (0.0046–0.0056 ng m-3 ppbv-1), suggesting that local sources are more important than those of long-range transport in this study.

CPF, CBPF and PSCF plots for TGM concentrations higher than the upper 25th percentile show high source probabilities in the direction of other industrial complexes including the Incheon port, and a coal-fired power plant as well as two national industrial complexes (Sihwa and Banwol).

TP-194

GASEOUS ELEMENTAL MERCURY (GEM) AND MERCURY CONCENTRATIONS IN BUILDING MATERIALS FROM THE FORMER HG-MINING DISTRICT OF ABBADIA SAN SALVATORE (SIENA, CENTRAL ITALY)

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Gaseous Elemental Mercury (GEM) concentrations and total and leached mercury contents on paints, plasters, roof tiles, concretes, metals, dust and wood structures were determined in the main buildings and structures of the abandoned word-class Hg-mining district of Abbadia San Salvatore (Siena, Central Italy), in order to understand how to proceed for the forthcoming remediation activities, the main aim being that to recover this site for museum and public green purposes. The mining complex covers a surface of about 65 ha and contains mining structures and managers and workers buildings. In this work, nine surveys of GEM measurements were carried out from July 2011 to August 2015 and more detailed measurements were performed in February, April, July, September and December 2016 in the buildings devoted to the production of liquid mercury. GEM concentrations showed a strong variability in terms of space and time mostly depending on the distance from the building hosting driers, furnaces and condensers and ambient temperature, respectively. Surveys carried out in the hotter period (from June to September) showed strikingly high GEM concentrations despite the fact that the mining activity stopped in 1982. In fact, in some of the contaminated sites GEM values reached concentrations that saturated (>50,000 ng m3) the GEM measurement device (Lumex 915+). Concentrations of total (in mg kg1) and leached (in g L1) mercury from different building materials, e.g. brick, rust, furniture, paint, plaster, concrete, showed for the same type of material highly variable values in dependence on the edifice or mining structure from which they were collected. Significantly high total and leached mercury concentrations, up to 46,580 mg kg1 and 4,470 mg L1, respectively, were measured. The obtained results are of relevant interest for the operational cleanings to be carried out during the reclamation activities. Operators are to wear appropriate personal protective equipments and act with machineries (e.g. hydro-blasters) to avoid the dispersion of GEM and reactive mercury in the environment during the removal of the building materials. This is highly recommended for both the operators safety and that of the inhabitants living nearby, the urban centre of Abbadia San Salvatore bordering the former mining area. Continuous acquisition of GEM data is suggested and samples of urine, blood and hair for mercury concentrations should be collected from the operators prior and after the reclamation since several months are likely necessary to complete the cleaning activity particularly in the most contaminated sites.

TP-195

AUNPS/TIO2NF: A PROMISING COMBINATION TOWARDS LOW COST AND EFFECTIVE SENSOR DEVICES FOR GEM MONITORING IN THE FRAMEWORK OF GMOS

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In the framework of ongoing research projects and programmes (i.e., GMOS, UNEP F&T) aiming to develop advanced sensors for major atmospheric pollutants, and having as overarching goal to assure a full operational capability of global observing systems for persistent pollutants such as mercury a novel sensors with promising sensing features for environmental applications have been designed and tested. The aim of this paper is to present novel kinds of sensors with promising sensing features for environmental applications, exploiting both the combination of gold affinity for mercury and nanosized frameworks of the sensing materials. Specifically, in the present study, conductive sensors working at room temperature and based on composite nanofibrous electrospun scaffolds of titania easily decorated with gold nanoparticles by photocatalysis under UV-light irradiation, have been developed to obtain nanostructured hybrid materials, capable of entrapping and detecting Gaseous Elemental Mercury (GEM) traces. The size and the shape of these nanostructures have been demonstrated to be key parameters in defining the properties of the resulting sensors, because of the strict relationship between the surface and the bulk of the sensing material which is extremely reduced in size. The increase in the number of binding sites has been confirmed to be a successful strategy to ensure sensitivity at trace level. SEM, AFM, TEM and HR-TEM analyses have been performed to characterise the morphology and the nano-sized structure of these composite materials. Different electrical and sensing features of the resulting chemosensors have been achieved by tuning fibres roughness and gold nanoparticle size. A suitable measuring chamber for mercury detection have been designed and developed in order to improve the sensing feature of the sensor. Thus few minutes of air sampling were sufficient to detect the concentration of mercury in the air without using traps (LOD ~ 1 ppb). Longer measurements allowed the sensor to detect lower concentrations of GEM (tens of ppt). A short thermal treatment (450°C, 3min) was necessary to completely desorb mercury from AuNPs. The resulting chemosensors are expected to be very stable over time, robust and resistant to the interference that may be caused by common solvents and by VOCs commonly present in ambient air.

TP-196

MERCURY BEHAVIOUR IN WASTE INCINERATION FACILITIES: GASEOUS TRANSFORMATIONS AND RETENTION BY CARBON AND MINERAL-BASED SORBENTS

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Waste incineration plants have been declared by the Minamata Convention as one of the major industrial sources of mercury (Hg) emissions. Elemental mercury (Hg0) is released from the incinerator (850-1200 ºC) into the flue gas and, as the temperature goes down, Hg undergoes a large number of homogeneous and heterogeneous oxidation processes. Hg0 is converted either to oxidized mercury (Hg2+) compounds and/or Hg adsorbed compounds (Hgp) onto particles. Effective and efficient mercury control technologies are needed to meet the increasingly stricter mercury emission regulations. Dry flue gas cleaning methods, using solid sorbents based either on soda or calcium hydroxide, are used in municipal solid waste (MSW) incineration but their efficiency on mercury removal needs to be further studied. Injection of activated carbon is a potential method for capturing mercury which is removed downstream, in a particulate matter control device, such as electrostatic precipitators (ESP) or fabric filter (FF). The efficiency of mercury removal from the flue gas is substantially affected by its speciation, flue gas composition and process conditions (e.g. temperature, air pollution control units). Many studies are found in the literature related to mercury behaviour under conditions of coal combustion, however, there is a lack of studies connected with MSW conditions. This study discusses the effect of temperature and gas components, present in typical flue gas from MSW incineration, on both mercury oxidation and capture by mineral and carbon-based sorbents. The study was carried out by means of a laboratory scale device that simulates the gaseous mercury behaviour in flue gas at temperatures ranged between 150-300 ºC. The results show the influence of HCl, SO2, NOx and H2O vapour in the gaseous transformation of mercury identifying the major reaction pathways. Under the simulated conditions, mercury (II) chloride (HgCl2), mercury (II) oxide (HgO) and elemental mercury (Hg0) are thermodynamically relevant species. In presence of CO2 and O2, the minor gas components NO, SO2, and HCl are involved in homogeneous oxidation of mercury and therefore, in the retention capacity. The higher temperature, the lower efficiency of Hg capture (i.e. higher emissions of Hg). SO2 is oxidized to SO3 at higher temperature. This effect, together with adsorption effects of CO2 and water vapour, inhibit mercury adsorption as there could be a competition for the same surface binding sites. The study provides a basis for the development of new strategies for mercury removal in the air pollution control devices of MSW incineration plants.

1a: Atmospheric mercury cycling and transformations: Insights from measurements and models

RP-002

QUANTIFYING SOURCES AND PATHWAYS OF MERCURY DEPOSITION AND EXPOSURE IN NORTHERN MAINE, USA USING INTEGRATED MODELING

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We examine the sources and pathways of potential mercury (Hg) exposure in the context of a case study involving the Aroostook Band of Micmacs based in Presque Isle, ME, using integrated modeling and data analysis. We use GEOS-Chem to quantify the sources of mercury deposition for Maine identifying the contribution of domestic, international, and historical sources , and the HYSPLIT trajectory model to provide further insight into source attribution. Simulated atmospheric concentrations are compared to measurement data for Hg at Presque Isle, ME. Average concentrations, seasonal variation, and diurnal variability are assessed and correlations (r2) calculated between observed and simulated time series. Simulated wet deposition from GEOS-Chem are also compared on a seasonal and annual basis to weekly samples from the Mercury Deposition Network at Caribou, ME. We examine source attribution under policy and no policy cases, identifying how observed atmospheric and wet deposition data would reflect these changes given variations in climate and other drivers. We show preliminary analysis of how these GEOS-Chem outputs can influence fish concentrations and ultimate exposure under desired levels of fish consumption.

RP-004

AIR MASS TRAJECTORY INFLUENCE ON MERCURY CONCENTRATIONS IN RAINWATER COLLECTED AT CAPE POINT, SOUTH AFRICA

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Mercury (Hg) is known to be a persistent and toxic heavy metal that can bio-accumulate in the aquatic environment and lead to serious human health effects. Hg is released into the atmosphere from both natural and anthropogenic sources, where in the atmosphere it can be present in a gaseous phase or in particulate matter. In the gaseous phase it can be incorporated with atmospheric precipitation (e.g. rainwater), which is the portion that eventually ends up in the aquatic ecosystem, leading to serious environmental problems. It is known that air trajectory calculations can be helpful in a variety of atmospheric analyses. It enables researchers to understand the transport of pollutants via trajectory routes, assisting in gaining a deeper understanding of pollution events, but more specifically of Hg in rainwater (wet deposition route). Ongoing research at Cape Point, South Africa has shown that most rain events are associated with cold fronts, for which approximately two-thirds reached the Cape Point observatory directly across the Atlantic Ocean from the south, while a third can be attributed to air mass movement from the Cape Town metropolitan region. Results to date collected for the rainy season between May to October annually (2007-2013), have shown that Hg concentrations range between 0.03 to 52.5 ng/L (overall average: 9.91 ng/L). A close relationship was also found between the GEM concentrations in air and TotHg concentrations in rainwater during the raining season. The work in this paper evaluated the existence of any relationships between Hg concentrations in rainwater, to the influence of meteorological variables such as wind direction and air mass backward trajectories. These variables will be valuable in understanding the ongoing monitoring of Hg in wet deposition at the sampling station.

RP-005

ATMOSPHERIC HG CONCENTRATIONS AT AN ALTITUDE OF 5240M AT CHACALTAYA STATION IN BOLIVIA

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A new regional station (CHC/GAW for short) of the Global Atmosphere Watch, which is part of the World Meteorological Organization (WMO), was set to work in December 2011 at Mount Chacaltaya (5240-5400 masl, 16°21.0´ S 68°07.9´). The purpose of this station is to monitor the atmospheric composition of the region, especially the greenhouse effect gases, reactive gases and particle material which is carried to the medium troposphere and to (or from the) free troposphere. To this purpose, a consortium of European and American institutions set up various instruments in the Cosmic Ray Laboratory.

From July 2014 to February 2016, we investigated atmospheric Total Gaseous Mercury (TGM) using a Tekran 2537A. The instrument worked with a 0.8 LPM flowrate and a sampling time resolution of 15 minutes. In addition to internal calibration using the internal permeation sources, the instrument was calibrated on site with manual injection of mercury vapors. The inlet, protected by a PTFE 0.45µm filter was situated 6 meters above the ground.

The TGM average over the period is around (0.65 ± 0.25) ng/m3 which is ~30% lower than other sites of the Southern Hemisphere (Amsterdam Island, Cape Point) where average TGM is around 1 ng/m3. Records of TGM in the tropical zone of the Southern Hemisphere are scarce, and this is the sole record at such a high altitude. These low values could indicate the existence of a TGM sink in this region, although further work is needed to determine its origin.

Atmospheric signal is partly influenced by polluted air masses from La Paz /El Alto urban areas during daytime due to convective transport of air masses to Chacaltaya station. At nights, aerosol and black carbon measurements clearly indicate that we have free-tropospheric conditions. We observe a clear seasonal feature, with higher TGM values during the rainy season (Oct to Jan) and lower values during the dry season (Jul-Sept). This data set will be useful to determine the influence of regional scale mining activities and the contribution of biomass burning occuring in the Amazon basin area.

RP-006

A CONTINUOUS RECORD OF ATMOSPHERIC MERCURY AT AMSTERDAM ISLAND, A BACKGROUND SITE OF THE SOUTHERN HEMISPHERE

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In the last few years continuous mercury monitoring has commenced at several sites in the Southern Hemisphere, providing new and more refined information. Under the frame work of the Global Mercury Observation System (GMOS) project, a monitoring station has been set up on Amsterdam Island (37°48′S, 77°34′E) in the remote southern Indian Ocean in January 2012.

For the first time in the Southern Hemisphere, a 3-year record of gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle-bound mercury (PBM) is presented. In 2016, the Tekran 1130-1135 unit was uninstalled, and we now record total TGM using a Tekran 2537B analyzer (1 LPM, 15 minutes). Wet deposition is also measured using an Eigenbrodt wet-only collector.

GEM concentrations are remarkably steady (1.03±0.08 ng m−3) while RGM and PBM concentrations were very low and exhibited a strong variability (mean: 0.34 pgm−3, range: This data set provides a new insight into baseline concentrations of mercury species in the Southern Hemisphere mid-latitudes and new measurement constraints on the mercury cycle, opening the way for new avenues in future modeling studies.

RP-007

INTERPRETATION OF NEW AUSTRALIAN MERCURY OBSERVATIONS USING THE GEOS-CHEM BIOGEOCHEMICAL MERCURY MODEL

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The GEOS-Chem biogeochemical Hg model (like every other major Hg model) has historically been developed and evaluated using observations from the northern hemisphere, which are significantly more abundant than observations in the southern hemisphere. A recent evaluation of GEOS-Chem against a global database of Hg observations found significant biases in simulation of Hg in the southern hemisphere; however, only three southern hemisphere sites were included and none were in Australia. To date, model performance in Australia has not been evaluated due to a lack of available Hg observations. Six years of continuous atmospheric gaseous elemental mercury (GEM) data have now been collected at the Cape Grim Baseline air pollution station located at the northwest tip of Tasmania. Additional time series of ambient GEM, ranging in duration from 1 to 3 years, have been measured at several locations in Australia: a tropical baseline site at Gunn Point NT, a site located near coal-fired power plants and open pit coal mining in Glenville, NSW, and an urban site in Sydney, NSW. These diverse, newly available atmospheric mercury datasets provide an opportunity to test our understanding of the Hg cycle in Australia as embedded in global models. Here, we will present evaluation of the GEOS-Chem model using the new Hg observations along with preliminary model development designed to improve model skill and utility in Australia. Our evaluations to date show that the model is able to simulate observed latitudinal gradients and seasonality, and that all Australian sites are highly sensitive to treatment of ocean Hg exchange. Uncertainties remain in simulating the southern hemisphere GEM background and the air-surface exchange over terrestrial Australian landscapes, and these are the focus of ongoing and future work.

RP-008

ESTIMATES OF DRY DEPOSITION OF SPECIATED MERCURY USING NATIONAL ATMOSPHERIC DEPOSITION PROGRAM GASEOUS MEASUREMENTS

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The National Atmospheric Deposition Program (NADP) and its Total Deposition Science Committee is planning to provide estimates of speciated mercury dry deposition using gaseous concentrations measured in the Atmospheric Mercury Network (AMNet). This poster will detail the approach that NADP will use, and provide basic output from this approach. The method will provide fluxes for the three operationally defined mercury forms, i.e., gaseous oxidized mercury (GOM), particulate bound mercury (PBM), and gaseous elemental mercury (GEM). Calculations will be made hourly to multi-hourly depending on availability. Weekly aggregated values (Tuesday to Tuesday) to align with wet deposition observation.

The flux of GOM is estimated as the product of its air concentration and dry deposition velocity calculated using the dry deposition scheme of Zhang et al. (2003; 2012).The flux of PBM is estimated as the product of its air concentration of both fine particulate (<2.5 µm) and an estimated course particulate loading (PBM 2.5-10 µm) and dry deposition velocity of fine and coarse particles calculated according to Zhang and He (2014). The flux of GEM is estimated using a bi-directional air-surface exchange scheme described in Wright and Zhang (2015).

Hourly Meteorological data used are from the archived Canadian weather forecast model at a horizontal grid resolution of 15 km by 15 km and surface and the first model-layer data (typically 40-50 meters agl). Land cover in the vicinity (3 km circle) of monitoring sites is taken from the MODerate resolution Imaging Spectroradiometer (MODIS) land cover type product (MCD12Q1). Fluxes for all existing land covers will be calculated and also aggregated into site-specific (land-cover area-weighted) values. Uncertainty in the estimated fluxes will be provided in the poster. At some point in the future, these estimates will be released for public use through its AMNet webpage.

RP-009

SEA SURFACE TEMPERATURE VARIATION LINKED TO ELEMENTAL MERCURY CONCENTRATIONS MEASURED ON MAUNA LOA

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The concentration of Gaseous Elemental Mercury (GEM) recorded at the Mauna Loa Observatoryin Hawaii between during the period 2002 - 2009 has been analyzed using theEmpirical Mode Decomposition technique.This technique has been used in numerous contexts in order to identify periodical variations in time series data.The periodicities observed in the Sea Surface Temperature collected by five buoys,three in the equatorial Pacific, and two to the south of Hawaii over the sameperiod are also observed in GEM concentrations measured at the MLO.The lag times in the observed periodicities are related to the position of thebuoys with respect to the measurement site. This demonstrates a direct link between climatological phenomena, in this case Sea Surface Temperature, and measured GEMand reflects the influence of ocean Sea Surface Temperature on GEM evasion. This is the first long-term experimental evidence of such a direct effect onGEM evasion from the oceanic surface driven by temperature.

RP-010

NEW TOWER INFRASTRUCTURE FOR MEASUREMENTS OF THE TEMPORAL MERCURY ATMOSPHERIC TRENDS IN KOŠETICE, CZECH REPUBLIC

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Climate, meteorology and atmospheric chemistry are scientific disciplines that study the same system: the atmosphere. Long-lasting research infrastructures covering all three areas are therefore of highest importance.

One of them, the Atmospheric Station (AS) Křen u Pacova (part of the National Atmospheric Observatory Koetice), central Czech Republic, is focused on monitoring of the occurrence and long-range transport of greenhouse gases, atmospheric aerosols, selected gaseous atmospheric pollutants and basic meteorological characteristics. The AS and its 250 m tall tower was built according to the recommendations of the Integrated Carbon Observation System (ICOS) and cooperates with numerous national and international projects and monitoring programmes. First measurements conducted at ground started in 2012, vertical profile measurements were added in 2013.

The Atmospheric Station (AS) Křen u Pacova consists mainly of a 250 m tall guyed mast of a lattice, 2.6 m wide triangular structure. It was designed and equipped exclusively for scientific purposes according to recommendations by ICOS, ACTRIS (Aerosol, Clouds, and Trace Gases Research Infrastructure Network) and GMOS (Global Mercury Observation System). Measurement data are or will be provided also to the InGOS (Integrated non-CO2 Greenhouse gas Observing System), EMEP (European Monitoring and Evaluation Programme), GAW (Global Atmosphere Watch) and ISKO (Czech Air Quality Information System) databases. The AS was built in 100 m distance from the Koetice Observatory, an infrastructure specialized in air quality and hydrological monitoring since 1988. The character of the site as rural background located in densely populated central Europe, far (> 80 km) from major pollution sources (cities, industry), has been confirmed in numerous studies using air quality data from the Koetice Observatory.

Atmospheric long-range transport is expected especially from the west and northwest, comprising also marine air masses as calculated for the Koetice Observatory.

The trends and gradient in atmospheric mercury concentration are part of this measurement programme. Station is equipped by the continuous gaseous elemental mercury (GEM) measurements conducted with two Tekran 2537B instruments installed in a ground-based container and in small technological container in height of 230m on the tower. This sampling design is worldwide unique, and is thoroughly examined and tested.

The detection limit and sensitivity of a Tekran 2537B instrument is < 0.1 ng m-3 (www.tekran.com).

The data sets produced during the period from the opening of this tower until now are now evaluated and validated. Tower represents very important infrastructure for the long-term atmospheric research and monitoring.

RP-011

PATTERN OF ATMOSPHERIC MERCURY SPECIATION DURING EPISODES OF ELEVATED PM2.5 LEVELS IN A COASTAL CITY IN THE YANGTZE RIVER DELTA, CHINA

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With the severe and persistent air pollution (e.g. extremely high concentrations of PM2.5), an emerging challenge is to understand pattern and sources of atmospheric Hg speciation during haze and non-haze days. Measurement of atmospheric mercury speciation was conducted in a coastal city of the Yangtze River Delta, China from July 2013 to January 2014, in conjunction with air pollutants and meteorological parameters. The mean concentrations of gaseous elemental mercury (GEM), particulate bound mercury (HgP) and reactive gaseous mercury (RGM) were 3.26±1.63 ng m-3, 659±931 pg m-3, and 197±246 pg m-3, respectively. High percentages of HgP during haze days were found, due to the increase in direct emissions and gas-particle partitioning of RGM. The average gas-particle partitioning coefficients (Kp) during moderate or severe haze days (PM2.5>150 ug m-3) were obviously decreased. GEM and HgP were positively correlated with PM2.5, SO2, NO2 and CO, suggesting a significant contribution of anthropogenic sources. Elevated HgP concentrations in cold seasons and in the morning were observed while RGM exhibited different seasonal and diurnal pattern. The ratio of HgP/SO2 and pearson correlation analysis suggested that coal combustion was the main cause of increasing atmospheric Hg concentrations. The monitoring site was affected by local, regional and interregional sources. The back trajectory analysis suggested that air mass from northwest China and Huabei Plain contributed to elevated atmospheric Hg in winter and autumn, while southeast China with clean air masses were the major contributor in summer. These results emphasized that both the reduction of anthropogenic emissions from local sources and regional cooperation policy among different city cluster were required to decrease Hg pollution in the atmosphere. Meanwhile, PM2.5 level in developing countries should be controlled to reduce the risks of atmospheric Hg to human health and land ecosystems.

RP-012

TWO YEARS OF GASEOUS ELEMENTAL MERCURY MEASUREMENTS AT AN AUSTRALIAN TROPICAL SITE

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The tropics represent an important region for mercury cycling as it is home to around 40% of the worlds human population, including over 50% of people under the age of 15 - a group at greater risk of adverse effects due to mercury exposure during early development. Stationary observations of gaseous elemental mercury (GEM) taken within the tropics are rare but report significant changes in concentration as source regions shift across hemispheres with the continual drift of the chemical equator. Initiated under the Global Mercury Observation System (GMOS) in June 2014, measurements of GEM are being undertaken at the Australian Tropical Atmospheric Research Station (ATARS) east of Darwin, Australia. The shifting latitude of the inter-tropical convergence zone (ITCZ) in this region leads to significant differences in air mass sources - identified using back trajectory analyses and concomitant radon measurements - over ATARS between the wet monsoon and dry seasons. Mean GEM concentrations over the entire year were 0.95 ng m-3, with higher values over the dry season (largely terrestrial fetch) than the wet season (greater oceanic fetch). GEM concentrations also showed a significant diurnal pattern, with a notable decrease overnight. Using radon as an indicator of atmospheric stability shows that this nocturnal depletion is enhanced under calm, stable boundary layers. Due to the low latitude of Darwin (12 ˚S), impacts from air masses originating in the northern hemisphere at this site are rare, however these events are characterised by increases in GEM concentrations. Back trajectory analyses show that these air masses pass over the populated Indonesian archipelago, suggesting impacts from GEM sources in this region rather than from the northern hemisphere background GEM pool.

RP-013

HOW HAS THE RELOCATION OF A MONITORING SITE CHANGED OUR UNDERSTANDING OF INFLUENCES ON RURAL ATMOSPHERIC MERCURY IN THE UNITED KINGDOM?

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Since January 2016, total gaseous mercury (TGM) has been monitored at Chilbolton, Hampshire, UK. Chilbolton became one of the UKs two EMEP supersites (Level II) in 2016 as a replacement for the Harwell Supersite, Oxfordshire, England. Chilbolton is operated by Ricardo-AEA on behalf of the UK Department for the Environment, Food and Rural Affairs. Mercury in air monitoring is undertaken at the site as part of the UK Eutrophying and Acidifying Pollutants (UKEAP) monitoring network run by the UK's Centre for Ecology & Hydrology. The monitoring site is in a rural setting surrounded by agricultural fields, a short distance from a small village and satellite observatory located at 51.144°N, 1.438°W.

Total gaseous mercury (comprising elemental and gaseous oxidised mercury) was monitored using a Tekran 2537A mercury vapour analyser, run at a resolution of 5 minutes, using dual channels allowing for continuous monitoring. The average TGM concentration at Chilbolton for January – October 2016 was 1.38 ng m-3, whilst the 2015 average for Harwell was 1.44 ng m-3. Both sites showing lower averages than the northern hemispherical background observed in other studies.

We present an initial overview of TGM measurements at the Chilbolton supersite since January 2016 and compares the data to that collected at the previous Supersite at Harwell between 2012 and 2015.

We have used wind sector analysis, cluster analysis and air-mass back trajectories in the OpenAir package in the R statistical software, we show how the TGM concentrations are influenced by local and regional sources (< 50 km) as well as long-range sources at both sites.

Previous work has shown that Harwell was significantly impacted by local sources, through its science campus location and potential mercury remissions due to activity on site, and from its relatively short distance from a coal-fired power station. We address the question of what new or different sources or influences (local or otherwise) are influencing TGM at Chilbolton? What effect has changing monitoring location had on the data? Are the sites comparable? How does that change the context and understanding of atmospheric mercury in the UK?

RP-015

DRY DEPOSITION FLUXES OF GASEOUS OXIDIZED MERCURY (GOM) AND PARTICULATE BOUND MERCURY (PBM): MEASUREMENT AND MODELING WORKS

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Mercury (Hg) is a toxic pollutant of concern throughout the northern hemisphere. Atmospheric Hg is often emitted as inorganic forms; however once inorganic Hg is deposited into aquatic ecosystems it can be transformed into MeHg, the most toxic form. Atmospheric deposition has been suggested as an important input for aquatic and terrestrial environments in many previous studies; therefore, quantification of atmospheric Hg deposition is critically needed in order to reduce MeHg levels in aquatic environment. Among atmospheric inorganic Hg species, gaseous divalent form (often called as gaseous oxidized mercury (GOM)) and particulate bound mercury (PBM) are considered to be important with respect to deposition due to high dry and wet deposition velocities although their concentrations are generally much lower than Hg0.

In this study, atmospheric concentrations of GOM and PBM were measured using KCl coated denuder and quartz filter, respectively. Size-distribution of PBM was also investigated using MOUDI sampler. Concurrently, a knife-edge surrogate surfaces using cation-exchange membrane and quartz filter were used to directly measure GOM and PBM dry deposition fluxes, respectively. The measured dry deposition fluxes were compared with the fluxes estimated using three-layer resistance model. Average concentration of GOM was higher in spring (7.47 ± 1.99 pg m-3) than in other seasons (2.76 ± 1.30 pg m-3). Average dry deposition flux of GOM was measured to be 0.74 ± 0.20 ng m-2 h-1 from surrogate surface, which was similar to the previous measurements in Yorkville (0.22 ng m-2 h-1) and Reno (0.79 ng m-2 h-1). There was a strong correlation between GOM concentration and GOM measured flux (R = 0.82), suggesting the rationality of dry deposition device. Measured flux was highly correlated with the estimated flux (R = 0.68); however, the measured flux was approximately 12 times higher than the estimated flux. Detailed results will be presented at the conference.

RP-016

TRAPSA (TRAJECTORY-BASED POTENTIAL SOURCE APPORTIONMENT): A GRAPHIC SOFTWARE FOR TRAJECTORY ENSEMBLE RECEPTOR MODELS AND AIR POLLUTION SOURCE IDENTIFICATION WITH GIS FUNCTION

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TraPSA (Trajectory-based Potential Source Apportionment) software is a graphical air pollution source analysis tool based on air pollutant measurements and a state-of-art air mass back trajectories modelHYSPLIT-4. TraPSA provides researchers and students an integrated, user-friendly platform for air pollutant database development and management, pollutant pattern and trend analysis, and potential source identification, by applying, comparing and exploring current popular trajectory ensemble receptor models. A database of pollutant monitoring site data can be established in TraPSA. The smart back-trajectory method in TraPSA helps users easily set up, calculate, and import trajectory data. TraPSA includes current popular algorithms for trajectory ensemble receptor models including Conditional Probability Function (CPF), Concentration Field Analysis (CFA), Concentration Weighted Trajectory (CWT), Residence Time Weighted Concentration (RTWC), Potential Source Contribution Function (PSCF), and Simplified Quantitative Transport Bias Analysis (SQTBA). TraPSA provides users sufficient GIS editing functions for mapping air pollutant source apportionment. In addition, GIS data files (ESRI shape file and Geo TIFF file) can be imported or exported by TraPSA allowing further research or editing by GIS software.

RP-018

CHEMISTRY OF THE BRHGO RADICAL FORMED IN THE BR-INITIATED OXIDATION OF GASEOUS ELEMENTAL MERCURY

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Some models of the global oxidation of gaseous elemental mercury (GEM) by atomic bromine suggest that BrHgONO is the major Hg(II) species formed. The molecular structure of this compound is analogous to that of HONO, which is known to photolyze rapidly to HO + NO. Quantum chemical calculations suggest that BrHgONO will photolyze in a similar manner to produce BrHgO + NO. The BrHgO radical has never been directly detected in the laboratory, although calculations a decade ago indicated that it is thermally stable.

In the absence of a way to produce and monitor the abundance of BrHgO, we use computational chemistry to evaluate its mechanism of reaction in the atmosphere. We estimate the rate constant for the reaction BrHgO + CH4 --> BrHgOH + CH3 to be 3 10-14 cm3 molecules-1 s-1 at 298 K. This corresponds to a BrHgO lifetime of 0.7 seconds with respect to forming BrHgOH. We are also studying analogous reactions in which BrHgO abstracts hydrogen atoms from ethane and formaldehyde. The theoretical approach used to date (PBE0 functional with a valence triple-zeta basis set) overestimates the rate constant for the analogous HO + CH4 --> HOH + CH3 reaction; as a result, the lifetime reported here is probably smaller than the true value. We are refining our results.

We find that BrHgO can also react with NO2 or NO to form thermally stable BrHgONO2 or regenerate BrHgONO, respectively. These reactions may be significant fates of BrHgO in areas heavily impacted by emissions from motor vehicles and energy production.

This work contributes to identifying the molecular identity of gaseous oxidized mercury (GOM) species formed in the Br-initiated oxidation of GEM. This work will help improve models of atmospheric mercury oxidation, aid laboratory scientists in designing kinetic and mechanistic experiments, and contribute to identifying GOM species in field work.

RP-019

INVESTIGATION OF ATMOSPHERIC MERCURY AT AN URBAN CAMPUS SITE IN TAIPEI, TAIWAN DURING 2007-2009

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Temporal variation of gaseous elemental mercury (GEM) was investigated over metropolitan Taipei in Taiwan during 2007 by using an in-situ Automated Gaseous Mercury Analyzer (AGMA). The mean GEM concentration was 4.3 ng m-3 with a range from 0.9 to 15.5 ng m-3. Distinct annual patterns were observed for the GEM with a winter maximum of 5.1±2.0 ng m-3 (n=3) and low in summer (3.7±1.1, n=3). The data showed the seasonal monsoons play a crucial role in the atmospheric long-range transport of Hg with its distribution and cycling in Taiwan. During the northeast monsoon in winter, air masses came from mainland China, bringing continental- and industrial-derived GEM to Taipei. The measured GEM/CO ratio of 0.0047 ng m-3 ppbv-1 is further similar to the results, which are observed at Mount Bachelor observatory (MBO) and Hedo Station, Okinawa (HSO) from Asian long-range transport. In contrast, the southwest monsoon prevailed in summer transports marine air from the South China Sea and west Pacific Ocean with lower GEM levels. Furthermore, a distinct diurnal variation of GEM concentration was observed, which level significantly exhibited greater in daytime than in nighttime during the warm season. Diel GEM variation was positively related to the ozone, PM10, PM2.5 and solar irradiance. The daily pattern with a maximum GEM concentration observed in the early afternoon and a minimum in the mid-night was likely due to local human activities, rising solar irradiance and ambient surface air temperature in Taipei area.

RP-020

THE WET DEPOSITION OF MERCURY, LEAD, DISSOLVED ORGANIC CARBON, AND MAJOR IONS AT THOMPSON FARM, DURHAM, NEW HAMPSHIRE USA

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Mercury is a naturally occurring metal that is toxic to many organisms. The atmospheric emission of Hg from natural and anthropogenic sources combined with the long atmospheric lifetime of gas phase elemental Hg and subsequent atmospheric deposition cause the element to occur globally in environmental systems. Atmospheric wet deposition of Hg via rain and snow is an important process in the biogeochemical cycling of Hg.

In an effort to characterize and understand processes contributing to the wet deposition of Hg, event based wet deposition samples were collected at the Thompson Farm AIRMAP site in Durham, New Hampshire from June 2006 to September 2009. Samples were analyzed for total aqueous Hg, total Pb, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate, ammonium, sulfate, sodium, potassium, and chloride. Statistically significant ($p<0.05$) positive correlations exist between concentrations of Hg and total Pb, DOC, TDN, nitrate, ammonium, sulfate, and potassium.

This multi-year dataset allows for seasonal comparisons between the analytes. Volume weighted mean (VWM) concentrations were highest during the summer for Hg, Pb, DOC, TDN, ammonium, and sulfate. The VWM concentrations of sodium, chloride, and potassium were highest during the fall. The lowest seasonal VWM concentrations of sodium and chloride were during the summer. The VWM concentrations for the majority of the other analytes were lowest during the winter. Seasonal patterns in total deposition, the product of concentration and total rainfall, largely follow the patterns in seasonal VWM concentrations.

The interpretation of these results may be used to distinguish atmospheric sources of Hg and inform efforts to model the atmospheric deposition of Hg.

RP-021

SOURCE, CONCENTRATION AND DISTRIBUTION OF GASEOUS ELEMENTAL MERCURY (GEM) IN THE URBAN ATMOSPHERE

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GEM was measured in downtown Toronto, Canada from Oct. 2015 to Oct. 2016 at two rooftop sites (i.e. KHN and JOR) which are 120m apart and have heights 29m and 60m respectively. Monitoring was done using mercury vapour analyzers (model 2537A, Tekran Inc., Toronto, Canada) accompanied with portable weather stations (Onset HOBOData Loggers) equipped with sensors to measure meteorological parameters.

The average atmospheric concentration of GEM was found to be 1.76 ± 0.87 ng/m3 at KHN and 1.23 ± 0.44 ng/m3 at the JOR site. The average GEM values measured at the two sites are statistically different at the 95% confidence level. This suggests local sources are contributing to the higher values measured at KHN. In addition, the difference in the height of the sampling sites and in city topography may also have contributed to the different values of Hg observed.

There is evidence of Hg pollution sources to the experiment sites from the NW and SE directions. Comparison of the data collected from KHN in 2004 and 2016 show similar Hg distribution patterns from the same direction but the average concentration observed at the sampling site dropped from 4.5 ng/m3 in 2004 to 1.76 ng/m3 in 2016. GEM measurements from downtown Toronto in 2004 and 2016 were also compared to background values from the CAMNet for the same or similar years. A decrease in average GEM was observed from 2004 to 2016 at both the urban sampling sites as well as at the rural CAMNet sites. The observed decrease of mercury may be a result of the restrictions placed on the use and disposal of mercury and mercury-containing products.

The results from the study suggest that the concentration and distribution of GEM in an urban environment is influenced by local and regional point sources, city topography and environmental policy.

RP-022

ATMOSPHERIC WET DEPOSITION OF MERCURY TO THE ATHABASCA OIL SANDS REGION, ALBERTA, CANADA

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Event-based wet deposition of mercury was collected in a study from 2010 to 2012 at the Patricia McInnes (AMS 6) monitoring site 30 km from the nearest upgrading facilities in Fort McMurray, AB, Canada. For the entire study period (21 months), volume weighted mean, VWM, concentration was 11.2 ng L-1 while total Hg wet deposition was 2.3 g m-2. Hg enrichment factors ranged from 105419 in rainfall, 45-599 in mixed precipitation and 73-266 in snowfall samples. Concurrent enrichment of trace elements including S, As, and Zn was also observed in samples. Our results suggest near field deposition of local anthropogenic emissions from the industrial and energy sectors impacted the AMS 6 site. Maximum Hg enrichment was found when winds transported smoke and particulate matter from forest fires 100 km away, to the sampling site. This finding corroborates previous findings that biomass burning is a source of particulate Hg that is deposited on a local scale. The magnitude of Hg wet deposition at the AMS 6 site was at the lower end of the measurement range made in the United States and Canada and limited by the low precipitation depths that occurred at this semi-arid location. This suggests that Hg dry deposition may be significant in the AOSR and should be addressed in future studies.

RP-023

TRENDS OF ATMOSPHERIC MERCURY AT CAPE POINT, SOUTH AFRICA, AND THEIR RELATION TO TRENDS OF OTHER TRACE GASES.

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Gaseous elemental mercury (GEM) has been measured at the WMO Global Atmosphere Watch (GAW) station, Cape Point, South Africa, since September 1995. Two techniques have been used: a low resolution manual technique until the end of 2004 and a high resolution auto-mated technique since March 2007. Besides meteorological parameters and solar radiation data, CO, CH4, CO2, O3, N2O and 222Rn concentration values are available for the interpretation of the GEM data.

A downward GEM trend was observed between 1995 and 2004 and an upward one since 2007. A statistical analysis of GEM, 222Rn, CO, CH4, and N2O trends as well as their inter-comparison will be presented. Furthermore, the implications of this comparison and possible underlying reasons of the observed trends will be discussed.

RP-024

LONG-TERM AIR MERCURY MONITORING AT LISTVYANKA STATION, SIBERIA

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The Listvyanka station is located at a shore of Lake Baikal, Siberia, far away from the existing mercury monitoring sites in Asia. Long-term air mercury monitoring within Global Mercury Observation System (GMOS) project started in October 2011. The station is part of the EANET network whereby numerous parameters of the air pollution, wet and dry deposition, as well as condition of the terrestrial and aquatic environment are measured. Lumex RA-915AM mercury monitor is used for the continuous air mercury monitoring in compliance with the unified GMOS network standard operational procedures.

The 5-years monitoring shows obvious seasonal variation of the background gaseous elemental mercury (GEM) concentration in air, which increases in the winter season with monthly average of 1.59 (1.43-1.79) ng/m3 and decreases in the warm season with monthly average minima of 1.25 (1.11 -1.54) ng/m3 in June-September. The same character of the seasonal variation is observed for particulate bound mercury (PBM) having average concentration of 6.2 (2.5-20) pg/m3.

Local short-term mercury concentration rises are associated mainly with the wind carrying air from industrial areas of Irkutsk and Angarsk cities where several big coal-fired power plants are located. These power plants are the main sources of the elevated acid gases and mercury concentrations in air measured at the Listvyanka site. A positive correlation between mercury, SO2 and NOX concentrations is observed both in the short-term variations and in the monthly average concentrations, whereas correlation between the mercury and ozone concentrations is negative due to the O3 depletion in the power plants plume. The short-term variations clearly show the possibility of the long distance mercury transfer with the so-called low-level atmospheric jets. In contrast to industrial emission, during huge forest fires of summer 2015, a positive correlation between mercury and ozone was observed. At the same time, no PBM increase was registered during the forest fires. Data processing reveals a moderate, statistically significant, diurnal cycle of the mercury concentration both in the warm and cold seasons with a lower level at night and higher level at daytime.

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RP-026

PASSIVE SAMPLING GASEOUS HG ACROSS THE GLOBE: HOW VARIABLE ARE SAMPLING RATES?

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Our recently introduced passive air sampler (PAS) for gaseous mercury (Hg) uses a radial diffusive barrier to control uptake kinetics and sulfur-impregnated activated carbon as a sorbent. Deploying multiple PASs simultaneously, retrieving them after variable lengths of time and analyzing them for the amount of Hg taken up yields an uptake curve. If the Hg concentration is simultaneously recorded with another sampling technique, e.g. a Tekran 2537 instrument, one can calculate a sampling rate SR (defined as the volume of air stripped of Hg per unit of time) from the slope of the uptake curve, i.e., by dividing the amount of Hg collected by the PAS by the actively measured concentration during the sampling period, and the deployment time. If a SR is known a priori, it is possible to compare the mean concentration measured by PAS with the actively measured concentration, i.e. establish the accuracy of the PAS. We previously presented a year-long uptake curve measured in Toronto, Canada, yielding a SR of 0.121 ± 0.005 m3 day−1. Here, we present year-long uptake curves measured at 22 sites across the globe with ongoing active Hg measurements. The sites, located in Canada, USA, Germany, China, Taiwan, and Australia, cover a range of climatic conditions (tropical to polar), geographic settings (city, mountain, coast) and Hg concentrations. The data are used in two ways. By calculating an air concentration using the SR determined in Toronto, we obtain an estimate of the accuracy of the PAS if it is assumed that the SR is the same everywhere. Alternatively, we can calculate site-specific SRs. We show that even with a generic SR, PAS-derived Hg concentrations are generally within 10 % of those obtained by a Tekran. Better accuracy can be achieved by using site-specific SRs. For sites for which no site specific SR exists a priori, it is possible to estimate a SR using local temperature and wind speed conditions.

RP-027

AMBIENT MERCURY SOURCE IDENTIFICATION AT TWO URBAN SITES: RESULTS FROM PRINCIPLE COMPONENTS ANALYSIS (PCA) AND CONDITIONAL BIVARIATE PROBABILITY FUNCTION APPLIED TO MERCURY MONITORING NETWORK DATA

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Gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM)) were continuously measured in Rochester, NY (NY43) and Bronx, NY (NY06) from Jan 2012 to Dec 2014. Continuous measurements of ozone (O3), sulfur dioxide(SO2), carbon monoxide(CO), nitrogen oxides(NOx), particulate matter (PM2.5), and meteorological data were also made at these sites. A principle components analysis (PCA) of 15 variables for the period identified several factors including wet deposition of GOM and PBM, and oxidization of GEM. Wood and coal combustion were found in two different factors through PCA analysis at the Rochester site and conditional bivariate probability function (CBPF) was used to determine the source of these two factors. A heating oil combustion factor was found for Bronx site indicating an increasing consumption of No.6 oil for central heating systems in that area. Mobile source was significant in 2012 but not in 2014 for both sites indicating the influence of the implementation of increasing tax of diesel starting in July, 2013.

RP-028

ATMOSPHERIC TOTAL GASEOUS MERCURY (TGM) CONCENTRATIONS AT A HIGH ALTITUDE SITE IN NORTHEASTERN UNITED STATES: CONCENTRATIONS AND RELATIONSHIPS TO OTHER POLLUTANTS

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A field campaign to measure total gaseous mercury (TGM) concentrations in ambient air was conducted at the Whiteface Mountain peak, NY from 1 June 2016 to 14 Oct 2016 using an automatic atmospheric mercury analyzer (Tekran 2537X) to investigate the concentrations at high altitude and relationships with other pollutants In addition concentrations were compared to a nearby low altitude site. The average TGM concentration from the high altitude site was 0.940.34 ng/m3, which is lower than the GEM concentration measured at nearby Huntington Forest ground site (NY20). A correlation analysis of TGM with other atmospheric pollutant concentrations was used to explore the characteristic of the measured TGM. In addition factors such as temperature, wind speed, wind direction and precipitation events were evaluated to determine if they are correlated with TGM concentrations. Conditional probability function (CPF) and potential source contribution function (PSCF) models were used to determine the source of TGM measured at the receptor site on the peak of Whiteface Mountain.

RP-029

USE OF A PARTICULATE MASS MEASUREMENT SYSTEM FOR TRACING POLLUTION AND MERCURY SOURCES USING LEAD ISOTOPES

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Tracing pollution sources in complex terrain, such as the western United States, is a difficult task. For this work, we investigated the hypothesis that lead isotope analyses would aid in identifying sources of mercury and ozone to the western United States. Reactive mercury and lead analysis of 24 h ambient air particulate matter was used to determine sources of pollution to three different sites in Nevada, USA. Measurements were made at three sites: a lower elevation, highway-impacted site (elev. 1370 m) from December 2013 to November 2015; a high elevation site (elev. 2515 m) adjacent to the lower elevation site from December 2013 to October 2014; and in Great Basin National Park (2061 m, eastern edge of Nevada near the Utah border) from March to October 2014. Ambient reactive mercury (gaseous oxidized mercury + particulate bound mercury) was collected using one inlet with cation exchange membranes while ambient lead samples were collected through a second inlet using Teflon membranes. A Tekran total mercury system (Model 2600) was used for analyses of CEM filters for total Hg. Lead isotope samples collected on the Teflon filters were analyzed with a multi-collector inductively coupled plasma mass spectrometer (IsoProbe). Lead isotope ratios have been used to identify Asian lead sources based on the 206/207 and the 208/207 lead isotope ratios. Analysis of preliminary results suggests that both higher elevation sites see a greater influence of Asian lead than the lower elevation site during the study periods. High Asian lead influence occurred mainly from March to June when long-range transport of pollutants occurs in this area. The two sites at higher elevation typically experience higher concentrations of reactive mercury during lower Asian lead influence, suggesting regional sources of reactive mercury. Reactive mercury at the low elevation, urban site varied less with the influence of Asian lead than the two higher elevation sites.

RP-030

A COMPARISON OF TOTAL GASEOUS MERCURY (TGM) CONCENTRATIONS MEASURED IN URBAN AND BACKGROUND AREAS IN SOUTH KOREA

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The objectives of this study were to: (1) characterize the hourly and seasonal variations of atmospheric total gaseous mercury (TGM) and co-pollutants concentrations in urban (Seoul) and background areas (Kanghwa island) of South Korea, (2) identify the relationships between TGM and co-pollutants concentrations, (3) characterize high TGM concentration events by distinguishing between long-range transport (LRT) and local impacts, (4) estimate TGM emission flux using ΔTGM/ΔCO, and (5) identify likely source locations of TGM for LRT events using potential source contribution function (PSCF) and likely source directions and locations of TGM for local sources using conditional probability function (CPF), conditional bivariate probability function (CBPF) and PSCF.

TGM concentrations were measured every 5 min from January 2008 to December 2009 on the roof of the Graduate School of Public Health building using a Tekran 2537A in the urban area and in Kanghwa island using a Tekran 2537B.

Hourly meteorological data and concentrations of SO2, NO2, O3, CO, PM10 and PM2.5 were obtained from the Korea Meteorological Administration (KMA) and the National Air Quality Monitoring Network (NAQMN), respectively. The TGM (3.7 ± 2.3 ng m-3), CO (661.7 ± 389.7 ppbv), NO2 (35.2 ± 17.5 ppbv), SO2 (7.4 ± 3.6 ppbv) and PM10 (52.5 ± 37.3 ppbv) concentrations in urban area were statistically significantly higher than the TGM (2.0 ± 0.9 ng m-3), CO (661.7 ± 389.7 ppbv), NO2 (35.2 ± 17.5 ppbv), SO2 (7.4 ± 3.6 ppbv) and PM10 (52.5 ± 37.3 ppbv) concentrations in background area ($p<0.01$). However, the O3 concentrations in the background area were significantly higher than those in urban area ($p<0.01$). The TGM concentrations in the background area were significantly positively correlated with CO, NO2, SO2 and PM10 ($p < 0.01$) but negative correlated with O3 ($p < 0.01$). Similarly, the TGM concentrations in urban area were significantly positively correlated with CO, NO2, SO2 ($p < 0.01$) and PM10 ($p < 0.05$) but negative correlated with O3 ($p < 0.01$).

A total of 150 high TGM concentration events in urban area were identified during the sampling period: 107 (71%) LRT events and 43 (29%) local events. A total of 91 high TGM concentration events in background area were identified during the sampling period: 61 (67%) LRT events and 30 (33%) local events.

Backward trajectory analysis starting from two sampling sites showed that air parcels arrived mostly from China for long-range transport events.

RP-032

MERCURY IN PUERTO RICO: HIGH DEPOSITION BUT LOW BIOACCUMULATION

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At a “clean air” trade winds site in tropical northeastern Puerto Rico, atmospheric total mercury (THg) deposition in 2006-2007 averaged 27.9 µg m-2 yr-1, higher than any site in the USA Mercury Deposition Network. These high rates of THg deposition are driven by high rainfall amount, and evidence also supports efficient capture of THg of upper tropospheric Hg by high rain-forming clouds. The elevated THg in deposition was reflected in high THg concentration and flux in streamwater, but assimilation into the local food web was quite low. There are few mammalian or freshwater fish predators on the island, but avian blood THg concentrations (n=31, from 8 species in various foraging guilds) ranged widely from 0.2 to 32 ng g-1, with a median of 4.3 ng g-1. Avian blood THg levels were an order of magnitude lower than comparable values in the northeastern U.S. These low levels were surprising given the high Hg inputs and watershed features that would seem to favor methylmercury (MeHg) production (Hg(II)-methylation) – high soil moisture, ample organic matter and sulfur, and year-round warm temperatures. However, organic soil (0-10 cm) along a hillslope to riparian transect averaged only 0.45 ng/g MeHg, with an average MeHg/THg ratio percent of only 0.34%. Stable isotope amendment incubations (n=6) to assess 200Hg(II)-methylation and Me201Hg demethylation

potentials along the upland to wetland transect indicated that rate constants for demethylation were 6-60 fold greater than those for Hg(II)-methylation, and calculated potential demethylation rates were 3-9 fold greater than Hg(II)-methylation rates. The net change in the ambient Me200Hg pool in the 6-day anoxic Me201Hg incubations revealed slight positive net methylation (mean = 15.8 ± 4.6 pg g-1 d-1 dry wt.; n = 6). This rate is considered an upper limit, as the soil samples were initially oxic (field Eh range +342 to +575 mV), while the 6-day incubations were performed under anoxic conditions. Thus, a likely resolution of the paradox is that MeHg degradation keeps pace with MeHg production on the landscape. The interplay of these microbial processes shields the food web from adverse effects of high atmospheric Hg loading on the island.

RP-034

ATMOSPHERIC SPECIATED MERCURY CONCENTRATIONS AT BACKGROUND SITE IN YANGTZE RIVER DELTA: INFLUENCE OF ANTHROPOGENIC SOURCE AND SUMMER MONSOON

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To better understand the influence of anthropogenic source and monsoon transport of atmospheric mercury(Hg) in Yangtze River Delta, measurements of total gaseous mercury (TGM), and gaseous oxidized mercury (GOM), particulate bound mercury(PBM) were carried out at Chongming Island (CM) in the eastern China from March 2014 to December 2016. The mean concentration (±SD) for TGM, GOM and PBM were 2.24 ± 1.17ng m−3, 14.12 ± 13.49 and 16.88 ± 31.69 pg m−3, respectively. In the sampling period, TGM showed an annual change trends from 2014 to 2016 with relatively lower concentrations (1.54±0.49 ng m-3) during 2016 and higher concentrations (2.81±1.46 ng m-3) during 2014. The Potential Source Contribution Function analysis suggests that the in-land source have a significant influence for GEM and PBM in CM while oceanic source contribute more for GOM. Back-trajectory-based analysis consistently indicated that TGM showed a monsoonal distribution pattern with relatively higher concentrations during the east Asia summer monsoon (EASM, from May to September) than winter monsoon. This study suggests that the anthropogenic source and monsoonal transportation have a collaborative significant influence for GEM in YRD. The EASM have a strong impact on long-range transport of Hg between YRD and east China sea. Besides the climate change in the study area, this study suggests that the decrease in anthropogenic emission also contributes to the down trend of mercury concentration at CM. The trajectory cluster analysis indicates that anthropogenic sources have more influences on the concentration variations of GEM compared to the summer monsoon. Various pollutants were also observed at CM and principal component analysis suggested that combustion emissions were the dominant anthropogenic mercury sources for the study area.

RP-035

ATMOSPHERIC GASEOUS ELEMENTAL MERCURY CONCENTRATIONS IN THE NORTH PACIFIC, NORTH ATLANTIC, AND CANADIAN ARCTIC FROM SHIPBOARD MEASUREMENTS

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Atmospheric concentrations of gaseous elemental mercury (GEM) were measured from a shipboard system during transects around continental North America and in the Canadian Arctic in 2009 and 2015.

In the Atlantic, strong diurnal variations were observed in GEM concentrations between 40°N to 23°N, which is consistent with previous work indicating high variability in the Atlantic basin. Concentrations in the Pacific between 9.5°N and 36°N were less variable, although minimum values were higher in the Pacific relative to the Atlantic. Concentrations of GEM were low in the equatorial Pacific and Atlantic, with the exception of the Panama Canal, where transient spikes in GEM concentrations were attributed to exhaust from Canal ship traffic.

In Arctic waters, GEM concentrations were elevated in Baffin Bay relative to the Beaufort Sea where concentrations were low throughout. Summertime atmospheric mercury depletion events (AMDEs) were potentially observed in the waters surrounding Banks Island, with consistently low observed GEM concentrations (< 1.0 nm m-3) observed over several periods.

The combined data set prevent us from distinguish between spatial and temporal differences to any great extent, although overlapping regions of the Beaufort Sea were measured in both 2009 and 2015. Southwest of Banks Island GEM concentrations were higher in late-June 2009 relative to late-August 2015 in contrast to previous studies, which generally have observed maximum GEM in summer.

Overall, our data provide insight into understudied regions of GEM distributions, especially Pacific and Canadian Arctic waters. In general, observed GEM concentrations are lower than both previously published shipboard measurements and averages collected at land-based monitoring sites. The temporal and spatial variability may inform models of GEM distributions in the marine boundary layer.

RP-036

OBSERVATIONAL EVIDENCE OF FORMATION OF GASEOUS OXIDIZED MERCURY IN THE TROPOSPHERE

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Within the EU-funded project, Global Mercury Observation System (GMOS) the airborne mercury species/fractions: Gaseous Elemental Mercury (GEM), Particulate Bound Mercury (PBM) and Gaseous Oxidized Mercury (GOM) were monitored using the Tekran speciation system at the R background measurement site on the west coast of Sweden. An evaluation of mercury concentrations measured during May 2012 to May 2015 is presented. The mercury concentrations measured at the R site were found to be low in comparison to other, comparable European measurement sites. The R site receives background air about 60% of the time. However, elevated mercury concentrations arriving with air masses from source areas from the south-east are noticeable. GEM and PBM concentrations show a clear annual variation with the highest values occurring during winter, whereas the highest concentrations of GOM were obtained in spring and summer. GOM concentrations observed at the R site often show a diurnal pattern with peak concentrations at midday. This phenomenon has also been observed at other sites and has often been interpreted as oxidation of GEM driven by local atmospheric photochemistry. An analysis of the origin of air masses arriving to the R site made it possible to distinguish between air masses associated to regional mercury sources from air originating from clean background air. This analysis showed that the highest GOM concentrations were observed in conjunction to import of air masses from the north which, are not associated with major anthropogenic mercury sources. The highest GOM concentrations were obtained from air masses originating from north of Scandinavia.

Here it is proposed that a significant part of the GOM measured during summertime at the R site is due to elevated concentrations of GOM accumulated in the free troposphere from oxidation of GEM. Evidence of this sort has also have been suggested from earlier observations, e.g. Wngberg et al., 2007; Weiss-Penzias et al., 2009. Hence, like with ozone, which also is secondary air pollutant the diurnal variation in concentration can be understood in terms of local meteorology, i.e. by nocturnal inversion at night, a phenomenon that occurs during clear sky conditions. During night GOM and ozone is depleted due to deposition on vegetation and on wet aerosols. The inversion prevents GOM and ozone from above to mix with the air below until the next morning when the inversion is broken by the sun and air from above are transferred to the ground through vertical mixing.

RP-037

IMPROVED REGIONAL PHOTOCHEMICAL MODEL SIMULATIONS OF SPECIATED AMBIENT MERCURY CONCENTRATIONS AND WET DEPOSITION

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Atmospheric mercury (Hg) deposition of three atmospheric mercury species gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM) is the largest atmospheric input to most terrestrial and aquatic ecosystems. Regional air quality models are needed to quantify Hg budgets in the atmosphere but limited by large uncertainties. The Community Multiscale Air Quality model with mercury (CMAQ-Hg) has been extensively used in research and policy-related studies. However, the default CMAQ-Hg (version 5.0.2) does not include GEM oxidation by active Br species, which have been suggested as important GEM oxidants. In this study, an algorithm depicting state-of-the-art Hg and halogen chemistry mechanisms was implemented in CMAQ-Hg, and Br species were constrained with an observed vertical BrO profile. Using this new mechanisms with initial and boundary concentrations (ICs and BCs) from global model output, we conducted simulations for the months of March to November 2010 over a domain covering the northeastern United States at a horizontal resolution of 12 km. Simulated GEM mixing ratios appeared to be dominated by the BCs, and hence reflected the significant seasonal variation that was captured in the global model output as opposed to the lack of seasonal cycles using the CMAQs default constant BCs. Our improved model simulations agreed well with GEM observations with 6.5% fractional bias (FB) in the fall, but underestimated GEM in the spring (FB = 13%) and summer (FB = 20%). GOM and PBM were better simulated using the improved model with FB = 2% and 19%, respectively, compared with FB = 72% and 69% using the default model. The new chemical mechanism alone resulted in a 12% decrease in GOM and a 34% decrease in PBM mixing ratios compared to the default one, and both reached maximum decreases in the summer. With simulated GOM and PBM close to or slightly higher than observations, Hg wet deposition was underestimated (FB = -60%) by the improved model at all observational sites in the domain. A sensitivity test of including GEM oxidation by OH in the new chemical mechanism resulted in the best simulations of monthly total Hg wet deposition with 0.3% bias.

RP-038

SOURCE - RECEPTOR RELATIONSHIPS FOR MERCURY DEPOSITION IN THE CONTEXT OF GLOBAL CHANGE

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There have been growing concerns on mercury pollution on local, regional and global scales. Better understanding of the source receptor relationships for mercury deposition in the context of global change is greatly needed. We use the global GEOS-Chem coupled atmosphere-land-ocean mercury model, driven by GISS ModelE2 meteorology to examine the source attribution for mercury deposition over various regions (such as North America, East Asia and the Great Lakes region) for the present-day as well as the impacts from future changes in anthropogenic emissions, biomass burning emissions, climate, land use and land cover. Through a suite of sensitivity simulations, we quantify the contributions from various sources (e.g., anthropogenic vs natural sources) and various regions (e.g., local emissions vs long-range transport) to the total mercury deposition over specific receptor regions. The spatial-temporal patterns of the perturbations to these source-receptor relationships associated with various factors in the context of global change are examined in detail.

RP-041

CHARACTERIZATION OF WET AND DRY DEPOSITION OF ATMOSPHERIC MERCURY TO A MOUNTAIN BACKGROUND SITE IN EAST ASIA IN 2009-2016

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Although East Asia is the major atmospheric mercury (Hg) emission source region, studies about atmospheric Hg deposition in this region are still limited. Here we reported the wet and dry deposition of atmospheric Hg to the Lulin Atmospheric Background Station (LABS), a tropical mountain site in central Taiwan (23.47ºN, 120.87ºE, 2862 m a.s.l.), from 2009 to 2016. Weekly rainwater samples were collected for total Hg analysis. Wet deposition flux was calculated by multiplying rainwater Hg concentration and rainfall depth. Concentrations of speciated atmospheric Hg, including gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM) and particulate Hg (PHg), were measured by the Tekran 2537A/1130/1135 speciation unit. Dry deposition of speciated Hg was estimated by multiplying concentration and deposition velocity. In 2009-2012, the annual rainfall ranged from 3172 to 4991 mm and the volume-weighted mean concentration of Hg in rainwater ranged from 8.71 to 13.53 ng L-1. Annual wet deposition fluxes ranged between 33.89 and 42.84 µg m-2. Hg wet deposition fluxes were higher in summer because of higher rainfall. Weekly wet deposition fluxes and rainfall were highly correlated ($R2 = 0.81$, $p < 0.01$). Annual dry deposition fluxes ranged from 67.41 to 75.91 µg m-2, nearly 2 times the wet deposition fluxes. Nighttime GOM dry deposition flux (6.92 µg m-2 yr-1) was higher than that of daytime (4.51 µg m-2 yr-1) due to higher GOM concentration and wind speed at night. Because of the high percentage of forest canopies at the monitoring site, average annual GEM dry deposition (59.71 µg m-2) was significantly higher than GOM (11.43 µg m-2) and PBM (0.13 µg m-2). It should be noted that the GEM dry deposition fluxes could be overestimated because GEM re-emission from the surface was not considered. We are still working on the estimation of dry Hg deposition using bi-directional surface resistance model. Moreover, we will expand the estimation of atmospheric Hg deposition to cover the whole 2009-2016 time period.

1c: Stable isotope studies of global mercury cycling and bioaccumulation

RP-043

DETERMINATION OF MEHG SOURCES TO FISH IN THE ST. LOUIS RIVER, MN, USA, USING HG STABLE ISOTOPES

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Mercury contamination in the Great Lakes region has become a prevalent concern due to elevated methylmercury (MeHg) levels in fish. While atmospheric deposition of Hg is ubiquitous, releases from legacy point-sources give rise to numerous Areas of Concern (AOCs) across the Great Lakes region. One of these AOCs is the lower St. Louis River estuary, which has MeHg concentrations in predatory fish double that of Lake Superior. Despite these highly elevated concentrations, it is difficult to infer the sources of the MeHg to these fish due to different Hg(II) inputs, as well as the complex ecology of estuarine systems. The aim of this study is to utilize Hg stable isotopes to elucidate sources of MeHg to populations of walleye and white suckers in the St. Louis River and Lake Superior region. Walleye from Lake Superior display enhanced Δ199Hg ≥ 5 ‰ and significant Δ200Hg = 0.08-0.10 ‰ for total Hg (THg) isotopes, likely from atmospheric influence and high levels of photochemical demethylation in the MeHg source. However, white suckers from Superior show depleted Δ199Hg and δ202Hg signatures and no significant Δ200Hg. This indicates that there are two distinct Hg sources for these fish in Lake Superior, presumably benthic and pelagic derived MeHg. In contrast to Lake Superior, the walleye and suckers feeding in the St. Louis River mirror the depleted signature observed in white suckers from the lake, which strongly suggests that Hg sources to these populations are obtained from the estuary and are likely sediment-based. While data supports sediment being the primary source of MeHg to fish in the St Louis River it still remains unclear whether the MeHg being produced is derived from legacy or more recent Hg (II), possibly of terrestrial or wetland origin. Preliminary data shows the presence of Δ199Hg (-0.12 ‰) and Δ200Hg (-0.05 ‰) anomalies as well as negative δ202Hg (-0.90 to -1.7) in upstream sediment THg commonly associated with precipitation and vegetation (litterfall). This signature is likely diluted downstream due to the high concentrations of legacy Hg (II) in the estuary and is not reflected in the bulk analysis of THg isotopes even though there is still a potential for methylation of this pool. In order to fully address the sources of MeHg to the St. Louis food web, further experiments examining the isotopic composition of MeHg pools in sediments and fish tissue will be performed.

RP-044

USE OF MERCURY STABLE ISOTOPE SIGNATURES TO ASCERTAIN SOURCES TO PISCIVOROUS GREAT LAKE'S FISH

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An important goal of the Great Lakes Restoration Initiative is to reduce fish mercury (Hg) levels such that advisories for human consumption can be removed. However, methylmercury (MeHg), the most toxic and bioaccumulative form of Hg, is the form that predominantly occurs in edible fish tissues. MeHg has a complex biogeochemical cycle in aquatic systems, and thus it is generally very challenging to offer effective scientific results that can lead to reduced MeHg levels in fish. Of particular importance is the ability to ascertain Hg sources, the relative bioavailability of those sources, and key processes controlling bioaccumulation in fish. Previous use of Hg stable isotopes (δ202Hg, Δ199Hg, and Δ200Hg) in sediments of the Laurentian Great Lakes allowed for the quantitative identification of Hg source portfolios for each lake. Here, we apply a similar approach to identify isotopically distinct Hg signatures in Great Lakes' piscivorous fish in order to evaluate Hg sources. Temporal variability and intra-lake differences in isotopic signatures were not evident, with the exception of Lake Erie, where fish collected in separate basins reflected distinct signatures. Additionally, concentrations of MeHg in predator fish did not correlate with isotopic Hg signatures or sedimentary total Hg concentrations. Great Lakes predatory fish span a large range of Δ199Hg (2.27 - 6.73‰) and displayed some of the highest odd mass independent fractionation (MIF) measured to date. The range in large odd MIF (Δ199Hg) may be explained by differences in euphotic depth (2-43m) among the Great Lakes, a region where Hg and MeHg may be entering the base of the aquatic food web at the lowest trophic levels. Signatures of even MIF (Δ200Hg), a potential binary tracer for precipitation, appears to be disconnected from local sedimentary sources in fish tissue, and is comparable in magnitude across five Great Lakes. This is particularly evident in Lake Ontario, where bottom sedimentary signatures suggest a significant contribution from past industrial sources, but the same signal is not evident in fish tissues. Our combined use of odd and even MIF Hg signatures allow us to evaluate the influence of atmospheric precipitation on bioaccumulation and compare the degree of photochemical processing of Hg in the Great Lakes.

RP-045

MERCURY RECOVERY FROM AQUEOUS SAMPLES FOR ISOTOPIC MEASUREMENT USING CHEMICAL PURGING AND CHLORINE-IMPREGNATED ACTIVATED CARBON TRAPS

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Measurement of stable mercury (Hg) isotope provides important chemical signatures for tracing the transport and transformation of mercury in the environment. However, such a measurement is challenging for natural water samples since typical Hg concentrations (0.5-100 ng/L) in these samples are at least 1,000 times lower than the needed level for isotopic measurements (>0.5 ng/ml) and therefore a pre-concentration step is required. Existing methods such as chromatographic method using ion-exchange resin or activated carbon,purge and trap method using gold trap or acid fixation. But those methods have the disadvantages such as inconsistent recovery, limited sample matrix, unsatisfactory precision and unsuitable for field deployment. In this study, we developed a pre-concentration method that uses modulated assemblies and can be deployed to field sites. The pre-concentration system include a 2.5-L bottle with a bubble diffuser, a chlorine-impregnated activated carbon (CLC) trap, a zero air filter was connected to the inlet, and a vacuum pump. Hg in aqueous phase samples is first oxidized by BrCl, then reduced with SnCl2. The produced Hg0 is purged from the aqueous phase and captured in the trap containing 500 mg of CLC. The captured Hg0 is then thermally desorbed in an argon carrying gas, followed by acid (4 M HNO3 and 1.3 M HCl) fixation. Complete purge and trap of Hg0 can be accomplished within 2 hours at 6 L/min flow rate of carrying gas. The method was verified using solutions spiked with NIST SRM 3133, UM-Almadén and BCR 482 standards at Hg concentrations of 1–200 ng /L. The results showed an analytical recovery of 98±2% (2SD, n = 45), with a deviation of d202Hg within±0.10‰ compared to the standards. The pre-concentration method represents a reliable and efficient method for determining the Hg isotope composition for natural water samples.

RP-046

INVESTIGATING METHYLMERCURY EXPOSURE IN NORTH ATLANTIC CETACEANS USING HG STABLE ISOTOPES

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Anthropogenic emissions have substantially perturbed the global biogeochemical cycle of mercury (Hg) and high latitude ecosystems are particularly vulnerable to Hg pollution and climate change. We investigated temporal changes in methylmercury (MeHg) exposures of long-finned pilot whales (Globicephala melas, n=68) between 1986-2015 using Hg isotopes (δ202Hg, Δ199Hg, Δ200Hg, Δ201Hg) as tracers of the physical environment and foraging ecology. Mass-independent fraction (MIF) of Hg (Δ199Hg, Δ201Hg) is mainly driven by photochemical demethylation in seawater. Enriched δ202Hg has been shown to result from demethylation. The ranges in Δ199Hg and Δ201Hg values in whales are similar across time periods with the exception of a few years following the 2010 volcanic eruption in Iceland that may have affected light penetration in surface waters. The mean δ202Hg values of whale muscle samples are consistently ~1.5 ‰ across the study period, which is ~1 ‰ higher than their prey (squid, blue whiting, and greater argentine). This fractionation is consistent with in vivo demethylation as a detoxification mechanism in the whales. Individuals with the highest MeHg concentrations in muscle have the lowest δ202Hg values and we hypothesize that this results from more limited MeHg demethylation. We further examine the Hg speciation and isotopes in livers to test our hypothesis. We find a linear relationship between Δ200Hg anomalies (-0.1 to 0.2‰) and Δ199Hg (R2=0.76) that has not previously been reported. Variability in Δ200Hg is thought to be driven by photochemical reactions in the tropopause and may provide an effective tracer for atmospheric Hg inputs to the ocean that are methylated and accumulated in aquatic biota.

RP-047

ISOTOPIC COMPOSITION OF ATMOSPHERIC SPECIATED MERCURY AT URBAN AND RURAL SITES IN KOREA: SOURCES AND TRANSPORT PATHWAYS

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Atmospheric mercury (Hg) species can be interconverted through various redox reactions, and this interconversion complicates the identification of the sources and transport pathways of Hg in the atmosphere. The Hg isotope signature is a useful tool for understanding Hg sources and the potential processes that Hg has undergone in the atmospheric environment. We examined the Hg stable isotope ratios in atmospheric Hg species (precipitation, gaseous elemental Hg, and particle-bound Hg) collected in Seoul (urban) and Taean (rural), Korea to identify the impact of local and regional transported Hg. We present both the mass-dependent fractionation (MDF, δ202Hg signature) and mass-independent fractionation (MIF) of odd (Δ199Hg signature) and even (Δ200Hg signature) Hg isotopes in precipitation, gaseous elemental Hg, and particle-bound Hg samples. Potential sources of Hg in atmospheric samples were identified by coupling the both MDF and MIF values obtained for Hg isotopes with a back-trajectory model.

RP-048

COMPARISON OF HG CONCENTRATION, SPECIATION AND STABLE ISOTOPIC COMPOSITION IN THE FOOD WEBS OF LAKE TITICACA AND LAKE URU-URU FROM THE BOLIVIAN ALTIPLANO REGION.

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Methylation and biomagnification of mercury (Hg) are well documented in most continental aquatic ecosystems. Few data exist in high altitude lake ecosystems, in particular from the Bolivian Altiplano region. This region is characterized by extreme physicochemical conditions (intense UV radiations and low dissolved oxygen contents) that were previously documented to favor in situ methylmercury production (Alanoca et al. 2016). Lake Titicaca and lake Uru-Uru are part of the endoreic Bolivian-Peruvian Titicaca catchment located at 3800m, and are connected together by the Desaguadero River. Lake Uru-Uru is located downstream of lake Titicaca, and is under the intense influence of mining activities.

Similar biological samples representative of the aquatic food webs from this region were collected in both lakes for assessing a meaningful comparison of Hg concentrations, bioaccumulation and stable isotopic composition. Biological samples included zooplankton samples, fish samples, in particular individuals of two native benthopelagic and omnivorous fish species (Orestias agassii and Orestias luteus), and of a pelagic piscivorous species (Odontesthes bonariensis). Blood samples from two endemic water bird species, Fulica ardesiaca (Andean Coot) and Rollandia roland (White-Tufted Grebe) characterized by omnivorous and piscivorous foraging behavior respectively were also collected in both lakes.

Total Hg concentrations increased significantly across the food webs in both lakes, illustrating the first evidence of Hg bioaccumulation in extreme lake ecosystems from the south American Altiplano region. Mercury concentrations were found to be 3 to 5 fold higher at each trophic level between lake Titicaca and lake Uru-Uru. This suggests that Hg levels in the food webs were directly related to the difference of in situ net production of Methylmercury (MeHg) at the base of each lake system. Lake Uru-Uru showed MeHg dissolved concentration of approximately 700±100pg/L, compared to 55±50 pg/L in lake Titicaca. This difference likely reflects a higher Hg methylation in lake Uru-Uru compared to Lake Titicaca where MeHg photodegradation is enhanced (confirmed by Hg stable isotopes analysis).

RP-049

HIGH VARIATIONS ON HG ISOTOPIC SIGNATURES IN BLOOD AND FEATHERS OF SKUA POPULATIONS FROM THE SOUTHERN OCEAN

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Seabirds bioaccumulate significant Hg amounts in their tissues as a consequence of their high position in marine trophic webs. Since they display contrasted foraging strategies, feeding on different trophic levels, marine birds are appropriate models to assess Hg biomagnification processes. Working on chicks is particularly interesting for tracing Hg contamination because they are fed with prey collected by their parents , who forage around the colonies during the breeding period. Therefore, chick tissues are mostly representative of Hg local contamination. Skuas are exceptional models to investigate since chicks' diet is largely composed of seabird meat and, consequently, they generally occupy a high trophic position within their communities. This study is focused on Hg speciation and isotopic composition of blood and feathers of Antarctic (Catharacta maccormicki) and subantarctic (Catharacta lonnbergi) skua chicks from diverse breeding colonies of the Southern Ocean (Adélie Land, Crozet and Kerguelen archipelagos and Amsterdam Island). Mass dependent fractionation (MDF, δ202 Hg) values for blood and feathers clearly discriminated subtropical, subantarctic and Antarctic populations. A quite significant correlation in δ202 Hg values (R2= 0.81) was found between both tissues. Nevertheless, a lower dispersion was found in the case of blood (mean SD δ202 Hg: 0.12 ‰) than in feathers (mean SD δ202 Hg: 0.22 ‰). This is especially remarkable in the case of Adélie population with blood δ202 Hg values varying from -0.02 to 0.41‰, whereas feather displayed values from -0.56 to 0.51‰. Concerning mass independent fractionation (MIF, Δ199Hg), feathers displayed highly dispersed values whereas Δ199Hg blood values presented a geographical trend from Antarctic to the subtropics. This dispersion effect may be attributed to different integration times between the two tissues studied. In conclusion, both blood and feathers are valuable bioindicators for Hg isotopic studies, however, blood samples seem to provide more specific isotopic signature to better discriminate different populations. Differences in Hg isotopic compositions in blood and feathers presented in this study highlight the capability of Hg isotopes in seabirds to investigate the factor controlling MeHg sources and biomagnification to the food webs of the southern marine ecosystems.

RP-051

NEW "IN-HOUSE" SECONDARY STANDARD FOR HG STABLE ISOTOPE RATIO ANALYSIS USING CVG-MC-ICP-MS

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Mercury (Hg) stable isotope ratio analysis (IRA) is nowadays widely used for determination of Hg sources and its biogeochemical cycling. Hg has seven stable isotopes, which fractionate during different biogeochemical processes. As a result of fractionation, specific isotopic signatures can be found in the end products, which can be further used for tracing Hg sources. Modern methods based on Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) enable total and species specific Hg isotopic analysis with high precision. As for all analytical techniques, a metrological approach is needed in order to assess and improve the quality of the results. Hg isotopic compositions are commonly reported as delta values relatively to the standard reference material NIST 3133. However, in IRA use of the secondary isotopic standard is very important. Nowadays, only few standards are used for quality control of isotope analysis. Due to the lack of Hg IRA secondary standards, current research is directed in producing 'in-house' Hg IRA secondary standard from cinnabar ore from Idrija mercury mine (Idrija, Slovenia). To get more information of elemental composition of that ore, neutron activation analysis has been done. In this work, storing conditions, different digestion ways (acid digestions, using 3 different acid mixtures, and high pressure asher), matrix effects and Hg stability were studied on Cold Vapour Generator (CVG) coupled with MC-ICP-MS. Results were compared in two laboratories using two different instruments. Negative mass-dependent fractionation (MDF) expressed as δ202Hg values of -0.90 ± 0.20 ‰ was obtained.

RP-052

FULLY PROGRAMMABLE ATMOSPHERIC HG ISOTOPE SAMPLING AND RESEARCH USING THE TEKRAN 1115I MULTI-VALVE MODEL AND 2537X ANALYZER

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Atmospheric mercury (Hg) monitoring programs such as GMOS , AMNet, CAMNet and the Chinese Hg program make observations of atmospheric Hg species concentrations, but do not provide direct information on Hg emission sources. Hg stable isotope studies of emission sources (coal, mining, natural, re-emission) and atmospheric

GEM have over the past decade shown great potential for better understanding Hg emission sources, and transformation and exchange processes in the atmosphere. The objective of this work was to develop a Hg isotope monitoring tool that is compatible with current mercury monitoring programs. The tool is based on the coupling of the new automated plug-and-play Model 1115i multi-valve module with the Tekran 2537X analyzer. The valve box, operated and programmed via a 2537X plug-in, routes analyzed Hg(0) at the 2537X cell vent into different channels where the Hg(0) is accumulated on traps. The traps are then manually desorbed for Hg isotope analysis by MC-ICPMS. We will present RD results on the use of gold traps and oxidizing solution traps, and illustrate results for diurnal Hg isotope monitoring. Potential applications other than diurnal monitoring are pollution-event (GEM, CO threshold) based valve switching, TGM/GEM Hg isotope monitoring using a pyrolizer, DGM/GEM isotope monitoring using an equilibrator, or gradient Hg isotopes using soils wells, snow or atmosphere towers, etc.

RP-053

A NATIONAL SURVEY OF TOTAL GASEOUS MERCURY ISOTOPE COMPOSITION

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With the 2011 promulgation of the Mercury and Air Toxics Standards by the U.S. Environmental Protection Agency, and the successful negotiation by United Nations Environment Programme of the Minamata Convention, global emissions of mercury (Hg) to the atmosphere from anthropogenic sources are expected to decline. Recent reports suggest regional gaseous Hg declines have already begun well before they were anticipated; however, providing independent evidence for the drivers of such declines is difficult. To address this challenge, the U.S. Geological Survey and National Atmospheric Deposition (NADP) program have initiated a national-scale effort to establish a baseline of total gaseous mercury (TGM) and Hg stable isotopic compositions at 31 sites distributed across North America. Samples were collected on gold traps and integrated over a 2-week period every other month using a simple static air pump. Collaboration with national scale air quality monitoring networks, such as the Mercury Deposition Network (MDN) and the Atmospheric Mercury Network (AMNet) has provided the backbone for linking the baseline to long-term wet Hg deposition and gaseous Hg monitoring sites, with approximately two thirds of the bulk air samplers operating at MDN or AMNet sites. The network includes a highly diverse set of sites ranging from remote locations (Denali National Park, Alaska) to highly urbanized sites (Bronx, New York and Boston, Massachusetts). For all sites, the average odd isotope mass independent fractionation (MIF) was -0.23‰ (D199Hg) and had a range of -0.38‰ to 0.01‰. We observed a positive correlation between D199Hg and D200Hg (r2 = 0.68). Mass dependent fractionation (MDF, d202Hg) was generally positive with a mean value of 0.27‰, although negative MDF was also observed at some sites. For example, near the highly contaminated Y12 Plant at Oak Ridge National Lab, Tennessee, d202Hg was consistently very light (-0.40‰), similar to co-located sediment. A comparison of urban vs background sites showed no difference in D199Hg, but there was a difference in d202Hg of 0.28‰ (urban sites consistently lighter). Differences in odd MIF and MDF among regions were small; however, there were interesting trends within some regions. For example, in eastern North America D199Hg was negatively correlated with d202Hg (r2 = 0.86). The long-term goal of this effort is to help provide a better understanding of anticipated future changes in atmospheric Hg concentrations and isotope abundances to evaluate the success of these regulations.

RP-055

ISOTOPIC CHARACTERIZATION OF MERCURY IN NATURAL GAS VIA ANALYSIS OF MERCURY REMOVAL UNIT CATALYSTS

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Natural gas (NG) represents an important and rapidly growing global energy source, and some commercially relevant reserves of NG are known to contain mercury (Hg) at concentrations between 0.01 and 5000µg/m3. The amount of gaseous elemental mercury released to the atmosphere from gas production and combustion is largely unknown, but is likely an increasing contribution to the global atmospheric Hg pool. Some models of changing sources of Hg to the atmosphere rely on Hg stable isotope compositions of atmospheric sources as baseline parameters. However, no Hg isotopic compositions have been published for Hg entering the atmosphere from NG. In an effort to characterize the isotopic composition of Hg released from NG, we analyzed the stable isotopic compositions of used mercury removal unit (MRU) catalysts (PURASPEC) supplied by Johnson Matthey Inc. MRU catalyst samples were analyzed from production facilities that process NG from different gas fields (Malaysia, North Sea, Brazil, N. Europe, Australia). Catalyst samples had a wide range of δ202Hg values (4.5‰) and a narrower but still large range of Δ199Hg values (0.74‰). We suggest that the bulk of Hg adsorbed to catalyst near the inlet of each MRU reactor is representative of the Hg isotopic composition of the NG source. Different gas fields range in δ202Hg and Δ199Hg from -3.75‰ to -0.68‰ and -0.09‰ to 0.65‰, respectively. Analysis of four samples from different positions within a single MRU reactor demonstrates significant fractionation of a small fraction of Hg that is not removed at the entrance to the MRU. We suggest that this fractionation is due to sorption of Hg to the catalyst surface from the gas phase, and that this process follows a Rayleigh fractionation model with ε ≈ -0.40‰. The Δ199Hg values of these samples decrease from inlet (0.25‰) to outlet (0.08‰), which suggests that the Hg sorption to catalyst surfaces may be causing mass independent fractionation related to nuclear volume effects of the sorption reaction. These results suggest that Hg isotopic analysis may be a feasible monitoring tool for Hg emissions from NG production in some gas fields. With further analyses of NG from around the world, a global average Hg isotopic composition could be estimated (as has been done for coal) to characterize this input to atmospheric Hg isotope models.

RP-056

MERCURY EMISSIONS AND ISOTOPE CHARACTERISTICS FROM CEMENT PLANTS

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Mercury emissions from two cement plants in China with pre-calcine technique were measured. Flue gas samples were taken with Ontario Hydro Method (OHM) and Hg within were detected with CVAAS (F732). Total Hg in solid samples such as limestone, Fe material, clay, coal, feed meal, ESP ash, clinker, cement products were determined with Lumex CVAAS. Hg isotope signatures in the flue gas and solid samples were detected with MC-ICP-MS (Nu Instruments, Nu plasma model II). Total Hg in the stack flue gas varied distinctively for two plants, with about 15 µg/m3 for plant #1, while <0.5 µg/m3 for plant #2, and most Hg were in divalent form. Hg emission factors were 76 mg Hg/ t clinker for plant #1 and 1.8 mg Hg/ t clinker for plant #2. Hg was introduced into the production system mainly by the raw material, such as limestone and Fe material, and coal constitute for another lesser portion (< 30%). Hg levels in the raw material and Hg cycling and accumulation ability in the system determined the Hg emission levels. Clinker contained no mercury, and Hg in the cement were introduced by additives, such gypsum and fly ash. No clear mass-dependent fraction (MDF) of Hg was found between raw material and flue gas samples, with δ202Hg in a range of about -1.3~-2.8‰, which were much lighter than the stack flue gas emitted from coal-fired power plants. Also, there were no mass-independent fraction (MIF) in different solid and flue gas samples.

RP-057

CHARACTERISTIC OF TOTAL MERCURY AND ISOTOPIC COMPOSITION OF HG IN WET DEPOSITION IN A COASTAL CITY IN SOUTHEAST CHINA

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Mercury has attracted a great concern because of its accumulative toxic effect to the organisms and human beings. Deposition of Hg from the atmosphere is regarded as an important source for aquatic and terrestrial ecosystem. Before that, mercury is subject to a series of physical and chemical processes in the atmosphere. Total mercury (THg) in daily precipitation was determined at four sites in a coastal city in Southeast China from June 2012 to May 2013. In addition, the precipitation samples during May-October (rainy season) and the rest of months (dry season) were respectively combined to examine the Hg isotopic composition. The volume-weighted mean concentration of THg ranged from 1.0 to 59.4 ng/L, with an annual value of 12.3 ng/L, and the wet deposition flux was 14.0 µg/m2/y. No significant difference of THg concentrations was observed between the rainy and dry seasons, which was inconsistent with the seasonal variation presenting higher THg in dry season due to increasing combustion in inland cities of China. A total of 8 mixed precipitation samples were first concentrated and then measured by MC-ICP-MS. All precipitation samples displayed the significant negative MDF (202Hg ranged from -2.2 to -1.5‰), the positive MIF of odd isotopes (Δ199Hg and Δ201Hg ranged from 0.08 to 0.22‰ and from 0.02 to 0.12‰ respectively), as well as the positive but not evident MDF of even isotope (Δ200Hg ranged from 0.01 to 0.07‰). The ratio of Δ199Hg/Δ201Hg was 1.10, being close to the ratio of MIF produced by magnetic isotope effect (MIE) but different from the value caused by nuclear volume effect (NVE), which suggested that MIE could be the main mechanisms during the aqueous Hg photoreduction. The Δ199Hg value in precipitation samples was quite low, and the correlation of δ202Hg and Δ199Hg was significantly negative, which indicated that the influence of long-range transport was small. The δ202Hg and Δ199Hg in precipitation and in some environmental samples from other studies were compared. The δ202Hg and Δ199Hg of all precipitation samples fell in the ranges in coal, but whether the coal combustion source could be considered producing the fractionation of Hg isotope was not sure because the fractionation of Hg isotope would be occurred during the process of coal combustion.

RP-059

MERCURY ISOTOPE RECORD IN SEDIMENTS FROM A REMOTE ALPINE LAKE IN WYOMING, USA

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Lake sediments provide an important record of changing mercury (Hg) deposition and isotopic composition. However, there are few records that preserve a record of direct deposition from the global Hg pool. A remote lake in northwestern Wyoming was studied because of its small watershed to lake surface ratio of ~2, and a lack of regional upwind Hg sources. The lake was cored and sectioned at 0.5 cm intervals. Organic soil and foliage were also collected from the watershed. The lake core samples were dated using 210Pb and 137Cs and analyzed for THg and Hg isotopic compositions including mass dependent (MDF) and mass independent (MIF) fractionation. THg concentrations ranged from 16.2 to 20.8 ng/g in pre-1850 samples before increasing to a maximum of 103 ng/g in 2005. Hg isotopic compositions of the lake sediments were relatively constant before 1850 with average values for δ202Hg (MDF), Δ199Hg (odd-MIF) and Δ204Hg (even-MIF) of -0.86‰, -0.02‰and

-0.19‰ respectively. Beginning in 1850, isotope values shifted toward recent sediment values for δ202Hg, Δ199Hg and Δ204Hg of -0.45‰, 0.47‰ and -0.41‰ respectively, which are similar to values measured in precipitation at other locations in North America. Soil isotopic values for δ202Hg, Δ199Hg and Δ204Hg are -1.69‰, -0.32‰ and -0.08‰ respectively, suggesting a negligible input of Hg from soil to lake sediments. Previous studies have suggested that the mechanisms responsible for MIF in precipitation are predominantly photochemical reduction (odd-MIF) and photochemical oxidation (even-MIF). Thus, the isotopic shifts that we observe are more consistent with changes in photochemical processes in the atmosphere rather than simply additions of anthropogenic Hg to the atmosphere.

RP-060

SEASONAL VARIATION IN MERCURY EXPORTED FROM AN UPLAND-PEATLAND ECOSYSTEM AS REVEALED BY STABLE MERCURY ISOTOPES

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Boreal peatland ecosystems are well known as an important sink of atmospheric mercury (Hg) as well as a source of highly toxic methylmercury (MeHg) to downstream ecosystems. Therefore, a thorough understanding of the complex Hg cycling in these northern ecosystems is warranted. Stable Hg isotopes were evaluated as a tool for investigating Hg cycling in an upland-peatland ecosystem. Specifically, we examined the variability of stable Hg isotopes in exported waters in a relatively well characterized small peatland-upland watershed (~0.1 km2, Watershed S2) in Marcell Experimental Forest in northern Minnesota. Exported water samples at the watershed outlet were collected biweekly when the stream flowed in years 2014 and 2015. Additionally, we collected surface and subsurface runoff from upland soils and porewater from the lagg zones, bog cores, upland soil, and litter. We determined total Hg concentrations and stable Hg isotope compositions for these sample types. Due to the high dissolved organic matter (DOM) in the exported waters, we completely oxidized the DOM by digesting the samples with 1-5% of an acidic mixture of KMnO4 and K2S2O8 at 95oC, before we purged and trapped the sample Hg by slowly adding SnCl2, and used 1% KMnO4 traps to collect reduced Hg. Data on exported waters over time (2014- 2015) showed a large range of mass-dependent fractionation (as δ202Hg, ranging from -2.1 to -1.3 ‰; n=21) but only a small range of mass-independent fractionation (as D199Hg, ranging from -0.35 to -0.10 ‰; n=21), with D199Hg resembling the isotopic values of Hg in bog and vegetation samples. Samples with more positive δ202Hg in the exported waters were collected during the spring snow-melt period, and these δ202Hg values were similar to the values of surface and subsurface runoff from the upland (i.e., -1.4 to -1.2 ‰; n=4). Our results suggest that the temporal variation of stable Hg isotope compositions in the exported waters is relatively large in this small upland-peatland watershed, which was largely driven by the hydrology of the watershed. The differences in δ202Hg values may allow us to distinguish two specific sources of Hg in the exported waters as derived from upland forest vs. peatland bog. Therefore, stable Hg isotopes could potentially be used in studying Hg cycling in DOM-rich surface waters, provided that effective methods are used to remove the influence of DOM on subsequent Hg extraction process (e.g., purge and trap) for high-precision isotopic analysis.

1d: Mercury cycling, bioaccumulation and health impacts in polar regions

RP-061

MERCURY ASSESSMENT AT INDIAN ANTARCTIC STATIONS IN ANTARCTICA – A PRELIMINARY STUDY

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Assessment of Mercury in Antarctica is important for many reasons: a. Antarctica is a pristine remote place which governs the climate of the southern hemisphere, and b. it has been decided in Minamata convention to reduce the risk of mercury pollution through research and monitoring. India is signatory to Minamata convention. Assessment of signature of mercury in remote location is also useful to understand the pathway of transportation so control mechanism can be derived by decision makers. Here, we present results of mercury monitoring in two Indian Antarctic Stations in years 2012, 2014-15 and 2015-16.

Maitri station is situated in Schirmacher hills in East Antarctica, around 80 km from the coast-line on rocky terrain. Schirmacher Hills cover approximate 35 km2 area with an average width of three km. It remains almost ice-free during austral summer; however, blizzards occasionally cover the rocky terrain with snow. Bharati station is located around 2500 km away from Maitri station in East Antarctica in the Larsemann Hills area. We recorded the Total Gaseous Mercury (TGM) in the atmosphere in Maitri by installing Tekran 2537-B mercury analyser during austral summer of 2012 during XXXII- Indian Scientific Expedition to Antarctica (ISEA). Observed values of TGM were in the range of 1 to 3.5 ng/m3. However, higher concentrations were recorded soon after after blizzard when concentration reached to nearly 10 ng/m3. During XXXIV- ISEA in austral summer of 2014-15 another instrument (Gardis-5) had been operated, near Bharati station for nearly 20 days and observed value sown the results in the Range of 1-to 2.5 ng/m3. Same instrument has been installed at Maitri station during austral summer of XXXV-ISEA (2015-16) and results recorded in the in range of 0.5 to 2 ng/m3.

Abrupt change in the concentration of the mercury soon after blizzard is a particular phenomenon that has to be further explored through experiments and observations. We will also present mercury concentrations in moss, water and snow samples from Maitri station to cover the complete biogeochemical occurrence of mercury in the area. These results can be used as baseline for future assessment of trends.

RP-062

WHAT VARIABLES ARE DRIVING THE VARIATIONS IN CONCENTRATIONS OF GEM, RGM AND P-HG DURING THE YEAR AT THE ZEPPELIN STATION ?

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Exposure of current levels of Hg in the Arctic can have adverse impacts on human health, particularly for the development fetus and children (AMAP, 2011). Long-range transported atmospheric Hg from sources in Asia, Russia, Europe and North-America, is recognized as one of the main antropogenic sources of this toxic pollutant in the Arctic, and especially focus has been on the impact of Atmospheric Mercury Depletion Events (AMDEs) as a means of delivering Hg to the ecosystems for now almost 20 years (Schroeder et al., 1998; AMAP, 2011). Mercury exist in the atmosphere mainly as gaseous elemental mercury (GEM) which has an atmospheric residence time of 6 months to 1 year. During AMDEs GEM can through a series of photochemically initiated reactions be oxidized to a more shorter lived species which is called reactive gaseous mercury (RGM). RGM can either stay in the air or if there are particles available be attached to these, and reported as particulate mercury (PHg). RGM and PHg can be deposited within hours to weeks. In the following presentation of five years of atmospheric speciation data for mercury from the Zeppelin station, Ny-lesund is presented. Speciated mercury have beens measured by automated Tekran mercury instrumentation. RGM was measured with a speciation unit (Model 1130) consisting of a KCl coated denuders while PHg was sampled on a particulate filter (Model 1135). In trying to find out what variables are driving the variations in concentrations of gaseous elemetal mercury (GEM), reactive gaseous mercury (RGM) and particulate mercury (pHg) during the year at the Zeppelin station five year of mercury speciation data together with meteorology data, aerosol data, UV data as well as correlation analysis have been studied.

RP-065

AIR SEA EXCHANGE OF MERCURY IN THE ARCTIC OCEAN

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Atmospheric deposition is the main input of mercury (Hg) to the ocean, even in remote locations such as the Arctic. Furthermore, evasion of elemental Hg (Hg(0)) is the major sink for oceanic Hg, resulting in air-sea exchange being an important part of the oceanic Hg cycle. Many factors influence gas exchange, and prior studies have suggested that some locations are net sources of Hg to the atmosphere, while others are sinks. To examine air-sea exchange in the Arctic Ocean we made high resolution measurements of Hg(0) in surface waters and Hg speciation in the atmosphere during the US GEOTRACES cruise in 2015 using sampling systems which continuously sampled surface water and the atmosphere. Additionally, samples were obtained for measurement of Hg in precipitation and aerosols, and for Hg profiles in sea ice. We use the measurements in water and the atmosphere to estimate fluxes of Hg(0) from the ocean to the atmosphere (these being potential rates for locations under ice). Overall, concentrations of Hg(0) were near saturation in ice free waters (21±12 fM), and resultant fluxes low, but Hg(0) was highly enriched under contiguous ice (120±101 fM, up to 450 fM), suggesting the continual formation of Hg(0) in waters even when ice covered. Predicted peaks in Hg(0) evasion, blocked by the sea ice barrier, were as high as 270 pmol/m^2/h. We compare our estimates of Hg(0) evasion with those of others and with models, and use these data, our measurements of atmospheric and ice concentrations, and the results of others to estimate potential deposition of Hg to the regions covered by the cruise. Based on these estimates, we can make predictions of the rate of response of the region to changes in ice cover and the potential impact of climate change on Hg dynamics and food web bioaccumulation in this important ocean region.

RP-066

DISTRIBUTION OF ELEMENTAL MERCURY IN THE ARCTIC AND ANTARCTIC SEA ICE ENVIRONMENT

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Due to climate change, the sea ice extents in the Arctic and in Antarctica are rapidly changing. Deposited atmospheric mercury onto surface snow and sea water that is not re-emitted back to air can enter the sea ice from the overlaying snow and/or the underlying seawater. Reported data on the concentration of total, elemental and methylated mercury species in polar sea ice is however scant.

Here we present concentrations of elemental mercury (Hg(0)) in various media in the Arctic and Antarctic sea ice environment. Samples of sea ice, snow, under ice water, brine, melt pond water, new ice and frost flowers were collected at 26 ice stations in the Eurasian and Amerasian Basins in the Arctic Ocean during the SWEDARCTIC 2016 campaign arranged by the Swedish Polar Research Secretariat (SPRS) aboard the IB Oden (8/8 – 20/9 2016). Corresponding samples were collected in

Antarctica at 25 ice stations in the Weddell Sea aboard R/V Polarstern (ANTXXIX/6&7, June - October 2013) arranged by the Alfred Wegener Institute (AWI) and in the Amundsen and Ross' Seas aboard IB Oden (OSO 10/11, SPRS, December – January 2010/2011).

The concentrations of Hg(0) in under ice water and in sea ice brine in the two polar regions were found to be comparable. However, the average concentrations of Hg(0) in sea ice were significantly higher in Antarctica (70 - 105 pg L-1) than in the Arctic (25 ± 10 pg L-1). The Hg(0) concentrations in the overlaying snow was also found to be considerably higher in Antarctica (250 - 730 pg L-1) than in the Arctic (10 ± 5 pg L-1), possibly due to spatial variations in atmospheric deposition and/or re-evasion.

A seasonal variation of the Hg(0) concentrations in the sea ice environment was found in Antarctica leading to the conclusion that factors such as solar radiation, temperature, brine volume and atmospheric deposition might be important for the transformation and transportation processes of mercury in sea ice in polar regions. The polar marine cryosphere, found to be a significant reservoir of mercury, is affecting the cycling of mercury in polar regions.Climate change and changing sea ice extent in the Arctic and Antarctica could lead to consequences for the global mercury budget.

RP-067

ACCUMULATION OF MERCURY AND METHYLMERCURY IN EMPEROR PENGUINS (APENODYTES FORSTERI) FROM THE WESTERN ROSS SEA, ANTARCTICA

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The emperor penguin (Apenodytes forsteri) is unique in that they are the only species breeding on the fast sea ice during austral winter months. Given that sea ice conditions are deteriorating significantly due to climate change, emperor penguins have recently been listed as near threatened species by the IUCN (the International Union for Conservation of Nature). Additionally, emperor penguins are the deepest divers reaching up to 500 m, which allows them to forage in a relatively wide range of water column. Because Antarctica is no longer free from impacts of anthropogenic activities and diving seabirds (e.g., penguins) play an important role in transporting not only nutrients but also contaminants from the oceans, there have been many studies on accumulation of contaminants including mercury (Hg) in different penguin species. However, there is very little information on Hg accumulation in emperor penguins. To the best of our knowledge, this is the first study reporting both total mercury (THg) and MeHg in emperor penguins from Cape Washington in the western Ross Sea, Antarctica. Liver and muscle samples were obtained from a total of 24 chicks and 6 adult emperor penguins. Our results fell within the ranges of previously reported Hg levels in Antarctic and subantarctic seabirds including penguin species. Compared to the muscle, both THg and MeHg concentrations in the liver were significantly higher, indicating that Hg detoxification as protective mechanism occurred. We found significant correlations of THg and MeHg with selenium (Se) in the liver only, suggesting a potential role of Se in Hg detoxification. Additionally, average THg and MeHg in chick penguins appeared to be somewhat higher than adults, likely due to molting as one excretory pathway of Hg to feathers. Further studies are required to investigate Hg accumulation process in emperor penguins and its controlling factors.

RP-068

CHARACTERIZING DIETARY METHYLMERCURY EXPOSURE IN SUBARCTIC FIRST NATIONS COMMUNITIES IN THE DEHCHO REGION OF THE NORTHWEST TERRITORIES, CANADA

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Fish are an important source of essential micronutrients for many populations, and serve as a cultural staple in traditional food systems of subarctic First Nations communities in the Mackenzie Valley. However, mercury is a common environmental contaminant often found in traditional foods including fish, and can pose health risks. This study measured total mercury (HgT) and omega-3 fatty acid (n-3 FA) content in wild-harvested fish of the Northwest Territories, and designed a dose reconstruction model to estimate community profiles of mercury exposure and n-3 intake. In 2016, a multi-year contaminant biomonitoring study was conducted to investigate contaminant exposure among First Nations communities of the Mackenzie Valley region.

The aim of this work is to build a draft, probabilistic model that will help evaluate the risk-benefit balance associated with consumption of locally-harvested freshwater fish. To achieve this goal, this study evaluated HgT and n-3 levels in harvested fish, and defined probability distributions for the draft model using profiles for HgT and n-3 FAs in fish tissue.

Samples from eight fish species were harvested in lakes of the Mackenzie Valley from 2013-2015. HgT in fish tissue was measured using a Direct Mercury Analyzer, and FAs were measured by lipid extraction and analysis using a gas chromatograph. Weight and dietary intake data collected from the Contaminants Biomonitoring Study were incorporated into the model. Biomarkers for community exposure to mercury and n-3 FAs will be used to gauge model performance.

HgT concentrations in predatory fish, including Northern Pike (0.458ppm), Walleye (0.467ppm), and Lake Trout (0.224ppm) were up to 8.65-fold higher than levels observed in benthivorous and planktivorous fish species, such as Cisco (0.054ppm), and Lake Whitefish (0.094ppm). Lake Whitefish demonstrated n-3 FA levels (288.87 mg/100g) that were up to 3.06 times higher than in predatory fish. Interestingly, significant negative correlations were observed between mercury and nutrient content in particular fish species. Negative correlations were observed between HgT and n-3 FA content for Burbot, Northern Pike, and Walleye. These associations will be built into the probabilistic analysis to refine the models ability to generate estimates for contaminant exposure and nutrient intake.

This model will be used to inform public health organizations in the development of consumption advisories for Northern First Nations communities, with the goal of minimizing the risks from Hg exposure while promoting the nutritional benefits of fish in traditional food systems.

RP-069

CLIMATE AND VOLCANISM CONTROLLED EXTREME MERCURY ACCUMULATION IN LIMNOPOLAR LAKE, ANTARCTICA, DURING THE LAST CA. 1600 YEARS

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The toxicity of its methylated forms and its ability of dispersion through the atmosphere make mercury (Hg) of special concern in remote-pristine ecosystems, such as the Artic and Antarctica. We sampled a short sediment core in Limnopolar Lake (Livingston Island, South Shetland Islands), spanning the last ~1600 years. Sediments were sectioned at high resolution, 210Pb dated and analysed for total mercury, as well as mercury species by means of Hg-thermo desorption-CVAAS. The core shows sections of extreme mercury concentrations ranging between 1,141 and 11,286 ng g-1 compared to background concentrations between 13 and 155 ng g-1Hg-thermo-desorption analyses indicate that mercury is retained in the sediment by organic matter at different stages of degradation. To explain the large differences in concentrations and the extremely high values found, we proposed a combination of different natural processes such as volcanism, climate and Hg depletion events. The nearby (30 km) volcano at Deception Island appears to be the main source of mercury, while climatic conditions have controlled freezing and thawing of ice-cover and snowpacks on the surface of the lake and in the catchment, which likely caused event based fluxes of Hg to the lakes sediments. Moreoever, extreme mercury concentrations match with elevated Br/C ratios (a measure of bromine deposition independent of the organic matter), suggesting that atmospheric depletion events may have been involved in enhanced mercury atmospheric deposition. These also coincided with low Total Solar Irradiance (TSI) during known low insolation periods. No evidence of anthropogenic mercury pollution was found.

RP-070

TEMPORAL TRENDS IN HG CONTAMINATION AND FOOD WEB TRANSFER ON A REMOTE ARCTIC ISLAND (BJØRNØYA, SVALBARD)

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The global release of Hg to the environment has increased greatly as a result of human activities. Since Hg is subject to long-range atmospheric transport, its continued global use and emission poses risks to humans and ecosystems both at the point of use and in remote locations. Bjørnøya, a remote Norwegian island in the Barents Sea, is an ideal location for research on Hg transport to the Arctic, given the presence of lakes supporting Arctic char populations that can act as reference sites where inputs are limited to long-range atmospheric transport (e.g. Laksvatn and Øyangen), as well as sites with a high abundance of seabirds (e.g. Ellasjøen), which may act as a biological vector for transport and deposition of Hg.

This work aimed to combine contemporary data with existing historical data and analysis of an extensive collection of archival fish samples in order to assess long-term changes in Hg contamination on Bjørnøya.

Briefly, we carried out Hg analysis on archival frozen muscle tissue samples from Arctic char collected from Bjørnøya over the past two decades. The sample set consisted of more than 500 char collected from 3 lakes (Ellasjøen, Laksvatn, Øyangen) over an 18-year period. We found that length-adjusted Hg concentrations were significantly higher in Ellasjøen than in either Laksvatn or Øyangen, likely reflecting elevated Hg inputs to Ellasjøen from seabirds, similar to what has previously been observed for PCBs. Hg concentrations in char from all lakes exhibited considerable interannual variability. For Ellasjøen, we observed a statistically significant increase ($P<0.00001$) in length-adjusted Hg concentrations of approximately 1.6 % per year. We also took a generalized additive modelling (GAM) approach in order to explore several key drivers of Hg concentrations in fish from Ellasjøen (n=218 fish), including collection year, length, age and condition factor. Using a GAM, we were able to explain approximately 80% of the deviance in fish Hg concentrations for Ellasjøen, with increasing Hg over time, a bimodal relationship between length and Hg (due to the inclusion of two char morphotypes in the sample set), a positive relationship with age, and a negative relationship with condition factor. We also explore potential drivers of the interannual variability and long-term increase in fish Hg in Ellasjøen by comparing our results with paleolimnological records of Hg in Ellasjøen, and long-term data on climate and seabird population size on Bjørnøya.

RP-071

DIURNAL VARIATION OF HG ABUNDANCE IN SURFACE SNOW IN CONNECTION WITH ATMOSPHERIC AND METEOROLOGICAL CONDITIONS

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Mercury deposition and re-emission from surface snow in the polar regions is an important part of the global mercury cycle. Mercury can be deposited during the polar winter and accumulate in the snow pack. During spring time the increasing solar radiation as well as the increase in oxidant species in the atmosphere can interact with the mercury present in the surface snow and increase emission of gas phase mercury from the surface. Dommergue et al. in 2014 suggested that atmospheric mercury above the Antarctic Plateau (Total gaseous mercury TGM) can undergo to a daily concentration cycle. Two 72 hours experiments were carried out in the proximity of Ny-Alesund research station, Svalbard. The two experiments were performed to evaluate the changes in concentration of Hg and other possible reactive elements in surface snow. The first experiment was conducted between the 27th and the 1st of May 2015 under 24h Sun irradiation conditions and the second was between the 7th and the 10th of April 2016 when a day and night cycle still occurred. The experiment was performed with high temporal resolution to investigate the possible changes in Hg, Br, major ions include nitrate, ammonia and I and trace elements. Surfaces samples have been collected every hour for 3 consecutive days, aimed at the study of the effect of solar radiation, snow events, deposition and meteorological conditions on surface snow chemical composition and evolution.

The results obtained were integrated with the meteorological data collected by the Amundsen-Nobile Climate Change Tower and compared with the TGM measured as part of the EMEP program at the Mt. Zeppelin Observatory in Ny-Alesund. The results show two different trends. During the period with continuous solar presence, no diurnal variations in surface snow were detected for Hg and other elements that can undergo photochemical processes. For the experiment conducted during the day and night cycle, Hg and I showed appreciable diurnal cycles with maximum concentrations during the night and lower concentrations during the daytime. During the 24h solar presence experiment, the surface snow mercury did not show any correlation with atmospheric mercury while with a cycle of light and dark conditions we detect a negative correlation between the two measurements. In both experiments snow deposition events occurred during the surface snow sampling. In both cases the Hg concentration in the snow increase markedly suggesting a primary role of snow deposition as a mercury scavenger from the atmosphere.

RP-072

A MODEL CALCULATION OF MERCURY CYCLES AT DOME CONCORDIA ON THE ANTARCTIC PLATEAU

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The remote Antarctic plateau receives significant inputs of mercury because this element is subject to long-range atmospheric transport and is readily cycled between surfaces and the atmosphere. Previous observational studies over the plateau have shown distinct diurnal and seasonal variations of mercury in near surface air, suggesting that a photochemically driven mercury cycle may occur at the air-snow interface. However, the controlling processes have not yet been well understood and quantified. In this study, we build a one-dimensional chemical and transport model and use it to simulate the mercury cycles over the year of 2013 at the inland French-Italian Concordia Research Station, in order to quantitatively explore the most important processes contributing to the mercury variabilities. The major chemical/physical processes in our model include the oxidation of gaseous elemental mercury (Hg0) by different oxidants (i.e. bromine, OH and ozone), the deposition of Hg0 and oxidized mercury (HgII) onto snow, the photo-reduction of HgII to Hg0 in surface snow, the reemission of Hg0 back into the atmosphere, and the exchange of boundary layer mercury with its free tropospheric pool. The transport is driven by vertical diffusion coefficients from a regional climate model which has been validated against meteorological observations at this station. Our model is constrained by in situ measurements of Hg0 and other chemical tracers at Dome Concordia in 2013. We find during the sunlit period that a bromine-initiated scheme oxidizes Hg0 quickly, favored by low temperature and high levels of nitrogen oxides. Sensitivity simulations suggest that the rate constant of Hg0 + Br and/or the mixing ratio of Br should be close to the upper uncertainty bound in order to match the observation. The recycling time for mercury in the surface snowpack is roughly one week but highly uncertain. During the austral winter, mercury levels in the shallow boundary layer are dominated by the exchange with the free troposphere. Our model simulations also reveal several specific research needs in order to obtain a better understanding of mercury cycling over the Antarctic plateau and other polar regions.

RP-074

THE ROLE OF MELTING ALPINE GLACIERS IN MERCURY EXPORT AND TRANSPORT: AN INTENSIVE SAMPLING CAMPAIGN IN THE QUGAQIE BASIN, INLAND TIBETAN PLATEAU

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Glaciers, particularly alpine glaciers, have been receding globally at an accelerated rate in recent decades. The glacial melt-induced release of pollutants (e.g., mercury) and its potential impact on the atmosphere and glacier-fed ecosystems has drawn increasing concerns. During 15th to 20th August, 2011, an intensive sampling campaign was conducted in Qugaqie Basin (QB), a typical high mountain glacierized catchment in the inland Tibetan Plateau, to investigate the export and transport of mercury from glacier to runoff. The total mercury (THg) level in Zhadang (ZD) glacier ranged from < 1 to 20.8 ng L-1, and was slightly higher than levels measured in glacier melt water and the glacier-fed river. Particulate Hg (PHg) was the predominant form of Hg in all sampled environmental matrices. Mercury concentration in Qugaqie River (QR) was characterized by a clear diurnal variation which is linked to glacier melt. The estimated annual Hg exports by ZD glacier, the upper river basin and the entire QB were 8.76, 7.3 and 157.85 g, respectively, with respective yields of 4.61, 0.99 and 2.74 µg m-2 yr-1. Unique landforms and significant gradients from the glacier terminus to QB estuary might promote weathering and erosion, thereby controlling the transport of total suspended particulates (TSP) and PHg. In comparison with other glacier-fed rivers, QB has a small Hg export yet remarkably high Hg yield, underlining the significant impact of melting alpine glaciers on regional Hg biogeochemical cycles. Such impacts are expected to be enhanced in high altitude regions under the changing climate.

2d: Mercury fate in aquatic and terrestrial food webs

RP-075

WHY IS MERCURY CONCENTRATION IN LARVAL SPIKETAIL DRAGONFLIES (FAMILY CORDULEGASTRIDAE) CONSISTENTLY GREATER THAN IN THEIR BURROWING RELATIVES, THE CLUBTAIL DRAGONFLIES (FAMILY GOMPHIDAE)?

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In North America, larval dragonflies are increasingly used as biosentinels for monitoring mercury (Hg) contamination in freshwater food webs. For practical reasons, field studies and monitoring programs alike often do not identify larval dragonflies below the taxonomic level of family. Several studies, however, have recognized that differences in Hg concentration among coincidently collected families do occur and may be associated with distinct family-level behavioral habits or guilds (e.g., burrowers vs. climbers). Understanding the consistency of these differences among guilds across habitats and water bodies will be important to the refinement of protocols using larval dragonflies as biosentinels. Apart from the implications for monitoring Hg, these guild differences generate basic questions about the intersection of environmental toxicology, behavioral ecology, and phylogeny. Two separate field studies conducted in the north-central states of Wisconsin and Michigan (USA) have shown consistent differences in total mercury (THg) concentration between two intraguild (burrower) families of late-instar larval dragonflies: the spiketails (Family Cordulegastridae) and the clubtails (Family Gomphidae). Across 5 of 6 water bodies, 3 streams and 3 lakes, THg concentration in spiketail larvae was significantly greater than in coincidently collected clubtail larvae. Furthermore, spiketail THg concentration was often greater than all other co-occurring larvae belonging to non-burrowing guilds (i.e., sprawlers and climbers). Mean (± SE) THg concentration across water bodies ranged from 170.9 ± 10.0 – 497.8 ± 136.2 ng/g dwt. and from 67.0 ± 2.1 – 165.0 ± 18.2 ng/g dwt. for spiketails and clubtails, respectively. In the 5 water bodies with significant differences, spiketail THg concentrations were between 189% and 558% greater than their clubtail counterparts. An explanation for these differences likely includes voltinism; in the north-central US, spiketails are merovoltine, spending 3 to 4 years as larvae, while clubtails are typically bivotline, spending 2 years as larvae. However, other factors including the amount of body setae (surface area), differences in burrowing behavior, and the significance of their phylogenetic relationship are explored.

RP-076

THG AND MEHG IN DOLPHINS (INIA SP.) OF THE MADEIRA RIVER BASIN, BRAZILIAN AMAZON

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In the Amazon, contamination by mercury (Hg) can be derived from: gold mining activities; Soil remobilization processes; and global Hg cycle. In aquatic ecosystems, Hg finds favorable conditions for organification and becomes methylmercury (MeHg), considered the most toxic chemical form of Hg, having the potential to bio-accumulate and/or biomagnify along the food chain. The red dolphin (Inia sp.), an aquatic mammal that inhabits the Amazonian rivers, can be considered a sentinel species of this environmental contaminant. The objective of this work was to evaluate the average level of total Hg (THg) and MeHg in Amazonian dolphins will be compared with the results of THg and MeHg in fish of the region collected along the Madeira river (Rondônia, Brazil). Without causing damage to the animal a simple biopsy was performed for the removal of small pieces of its fatty tissue and soon after, these were returned to the river. The THg and MeHg determinations were performed by cold vapor atomic absorption spectrophotometry and by gas chromatography coupled to atomic fluorescence spectrometry, respectively. The results of THg (n=19) and MeHg (n=65) in red dolphins presented an average of 0.9408 ± 1.0515 mg/kg and 0.6904± 0.5546 mg/kg, respectively. Average THg concentration in fish muscle tissue (n=320) was of 0.3665 ± 0.4858 mg/kg and for non-carnivores 0.3648 ± 0.4857 mg / kg. The results show the dynamics of mercury, where the bulk is in the form of methylmercury (HgT: MeHg ratio of 61%). Carnivorous fish presented higher results than non-carnivorous fish and, consequently, because the porpoises have a diet almost exclusively food in fish and because they are food web tops, showed higher concentrations of HgT and MeHg than carnivorous fish, Result already expected due to biomagnification and bioaccumulation of this contaminant along the trophic chain of resident organisms of the Amazon region.

RP-077

CONCENTRATIONS OF MERCURY IN TROPICAL CATFISH FROM SINNAMARY RIVER ESTUARY IN FRENCH GUIANA (SOUTH AMERICA)

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Mercury is rarely measured in fish from tropical river estuaries but local people rely on these for food. In tropical regions, mangrove forests provide an important nursery for juvenile fish and are used as a habitat by a variety of other aquatic and terrestrial animals. In French Guiana and neighboring countries, there are several factors that could contribute to elevated methylmercury concentrations [MeHg] in estuarine fish: 1). the soils in the Amazon are naturally enriched with Hg; 2). streams and rivers in some areas have been a subject to Hg pollution from small scale artisanal gold mining; 3). A reservoir, Petit Saut, created at time of hydroelectric dam installation upstream Sinnamary River, sources MeHg for downstream. We therefore asked whether fish in the lower part of the estuary have elevated [MeHg] and whether their consumption would pose health hazard to people. During the dry season in October 2015, we have sampled fish by gill net in the mouth of the Sinnamary River Estuary (SRE; 5.45°N 53.01°E), where salinity ranges from ~2 to 32 and where the evolving marine mangrove (Avicenia sp.) forest hugs the river bank. Two catfish species Hexanematichthys proops and Aspistor quadriscutis dominated the 2-day catch (n=28 and 43, respectively) with total lengths ranging from 42 to 67 and 41 to 53 cm, respectively. Other adult fish species e.g. Hexanematichthys couma, Sciades herzbergii, S. passany, Macrodon ancylodon, Cathorops spixii, C. arenatus, Lobotes surinamensis, Pellona flavipinnis, Centropomus undecimalis, C. mexicanus, C. ensiferus, Pseudochenipterus nodosus, Cynoscion acoupa, as well as their juveniles, shrimp and crabs (Uca maraocani) were also collected to establish mercury concentrations in the food web of this ecosystem. Overall, the mean total [Hg] in the muscle tissue were ~ 2-fold higher in H. proops (mean= 0.42; range: 0.17 – 1.34 mg kg-1 wet wt.) in comparison to A. quadriscutis (mean= 0.18; range: 0.03 – 0.47 mg kg-1 wet wt.). The average % MeHg was ~50 for both catfish species. [MeHg] in the other large fish fell within the range of values observed for the above-mentioned catfish. Among all analyzed fish, none exceeded the MeHg safety levels in France (i.e. 0.5 mg kg-1 wet wt.). We therefore conclude that despite a risk of elevated MeHg in fish of SRE, observed [MeHg] were low and catfish of size comparable to that in this study are safe to eat.

RP-078

RE-WRITING HISTORY: FIVE DECADES OF METHYLMERCURY CONCENTRATIONS IN AQUATIC ZOOBENTHOS FROM LAKES IN THE NORWEGIAN BOREAL ECOZONE

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A major key to understand the Hg contamination of aquatic biota is the exposure of toxic and organic forms (i.e. methylmercury, MeHg) of mercury (Hg) at the base of the food web, and transfer through consumer trophic levels. While data series of historical Hg concentrations in top consumers of aquatic food webs (e.g. fish, birds) are increasing in peer-review literature, long-term high resolution datasets of Hg in biota from lower food web compartments are scarce. In the present study we tested the hypothesis that long-term changes in MeHg in biota relate to water chemistry and are indirectly linked to climate and deposition change.

We have, through access to historically archived samples, analysed MeHg in samples of littoral macro-invertebrates from two Norwegian boreal lakes, Breidtjern (59.60 N, 11.40 E) and Langtjern (60.37 N, 9.73 E). Breidtjern and Langtjern are both humic lakes with relatively similar water chemistry (data from 2016): total organic carbon concentrations between 10 and 15 mg/L; pH approximately 5.0; total Hg concentrations between 2.5 and 6.5 ng/L; and MeHg concentrations between 0.02 and 0.2 ng/L. The historical samples we analysed date back to 1976 and 1978 for the two lakes, respectively, with samples collected with a frequency of between every second and every fifth year, and yearly after the millennium. We also sampled present-day invertebrates from the two lakes and quantified transfer of aqueous MeHg to the invertebrates (as bio-concentration factors, BCFs). The historical invertebrates are primary and secondary consumers, taxonomically described and fixed in ethanol. Literature suggests that ethanol affects lipid content and therefore stable isotopes, but not MeHg which is primarily associated with proteins. The possible effects from sample storage over time in ethanol solutions were tested by quantifying leakage of MeHg from present-day invertebrates stored over 500 days.

Our study will show if and how records of archived invertebrate samples can be used to untangle historical time-trends of Hg concentrations in boreal lakes. We will, in combination with explanatory variables, highlight the changes in Hg concentrations that can be found with time in these lakes. Included explanatory variables, water chemistry, hydrology, and precipitation, will be used in a statistical analysis of MeHg in primary consumers, similar to an earlier analysis of DOC time series.

RP-079

FRESHWATER TURTLES AS BIOMONITORS OF MERCURY AVAILABILITY IN AQUATIC ECOSYSTEMS OF WESTERN TENNESSEE

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Turtles are often used as biomonitors in aquatic ecosystems as they are long-lived top predators making them highly susceptible to both bioaccumulation and biomagnification of mercury. The purpose of this study was to determine mercury exposure in three species of turtles, the red-eared slider (Trachemys scripta), the common snapping turtle (Chelydra serpentina), and the alligator snapping turtle (Macrochelys temminckii), in aquatic ecosystems across western Tennessee. All three species of turtles were trapped at twelve different sites from March to July 2016. Toenails were taken from the back feet of each captured turtle and analyzed for total mercury using a Nippon MA-3000 Direct Mercury Analyzer. Mercury exposure varied significantly among species: alligator snappers (5.26ppm)>common snappers (4.49ppm)>red-eared sliders (1.09ppm). Mercury concentrations in both alligator and common snapping turtle toenails exceeded the EPA recommended consumption level for freshwater fish (0.3 ppm). This is of particular cause for concern from a human health perspective as common snapping turtles are still harvested for human consumption in this region. Mercury concentrations in turtle toenails are a strong predictor of soft tissue and organ concentrations suggesting consumption of common snapping turtles from this region may pose a human health risk.

RP-080

METHYLMERCURY BIOACCUMULATION IN VERNAL POOL INVERTEBRATES

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Vernal pools in Northeast US forests provide critical habitat for numerous invertebrate and amphibian species. However, vernal pools have also been shown to be potential “hotspots” for accumulation and methylation of mercury (Hg). Under the right conditions, the MeHg produced within the pool can bioaccumulate in the vernal pool organisms, which can subsequently become a vector for MeHg transport into the surrounding terrestrial ecosystem. During the spring of 2015, 20 vernal pools in Vermont were sampled for common invertebrates using funnel traps or hand collection. The pools ranged from Rockingham, VT north to Walden, VT, all east of the Green Mountain range, and were influenced by a variety of forest types and land uses. Invertebrate samples were analyzed for MeHg or total Hg concentration, as well as δ13C and δ15N. There was large variation in MeHg concentration across all of the pools. Caddisfly larvae (MeHg range: 6 – 189 ppb DW; 14 pools) and mosquito larvae (MeHg range: 4 – 243 ppb DW; 8 pools) were generally lower than fairy shrimp (MeHg range: 71 – 283 ppb DW; 7 pools) or predatory beetles (Acilius sp. THg range: 51 – 613 ppb DW; 10 pools, Dytiscus sp. THg range: 131 – 342 ppb DW; 6 pools). δ15N of predatory beetles was generally higher than that of fairy shrimp, caddisfly, or mosquito larvae, as expected. Relationships between pool and landscape characteristics and Hg bioaccumulation in resident invertebrates will be discussed.

RP-081

SPATIAL VARIATION OF METHYLMERCURY CONCENTRATION IN MEDITERRANEAN SEA ZOOPLANKTON, FISH AND, SQUID

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Plankton and lower trophic level nekton are critical conduits for the transfer of methylmercury (MeHg) in marine food webs, yet little is known about the variation in MeHg concentrations between species and across sites in these lower trophic fauna. Zooplankton were sampled from the neuston layer at both coastal and open sea stations in the Mediterranean Sea during cruise campaigns undertaken in the fall of 2011 and the summers of 2012 and 2013. Horse mackerel and two species of squid were obtained opportunistically during the same cruises. Zooplankton were separated by morphospecies, and the most abundant taxa analyzed for methylmercury (MeHg) concentration. Squid and fish samples were analyzed for total Hg (THg). Data will be presented for euphausiids, mysids, and myctophids, all important prey items for fish, marine mammals, and birds, as well as for the mackerel and squid. Euphausiid MeHg concentration ranged from 22 226 ppb DW with spatial variation between sites. Myctophid MeHg tissue concentrations were similar, ranging from 22-297 ppb DW across all sites, while mysid concentrations were slightly lower (range: 6 204 ppb DW). The data suggest elevated MeHg concentration in the Tyrhennian and Balearic seas in comparison with more eastern and western stations. Horse mackerel had higher muscle tissue concentrations (range across sites: 344 - 1510 ppb DW) on average than flying squid (range: 49 448 ppb DW), with some individuals exceeding the EPA 300 ppb WW tissue criterion. Euphausiids, due to their abundance, larger size, and importance as a food source for other fauna may be a good species to use for MeHg monitoring in marine systems such as the Mediterranean Sea.

RP-082

EVALUATION OF CHRONIC NONCOMMUNICABLE DISEASES POTENTIALLY RELATED TO MERCURY CONTAMINATION IN A RIVERINE POPULATION OF THE AMAZON

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The presence of mercury of anthropogenic and natural origin in the aquatic ecosystems of the Amazon represents an exposure factor for neurotoxic, teratogenic and chronic noncommunicable diseases. In the Amazon region, contamination by organic and inorganic mercury can be attributed mainly to high fish consumption and to the practice of goldmining, respectively. The methylmercury levels in humans can be considered an endemic condition in Amazon, mostly in traditional populations such as the riverines and Indigenous , by the expressive daily consumption of fish, as well as cassava flour, chestnut and sometimes meat. However, changes in the livelihoods of these populations, due to political, economic and social factors, have been influencing the human health and the environment, due to the insertion and possible exclusion of risk factors and protective factors, respectively. According to the World Health Organization, diabetes mellitus, metabolic syndrome, overweight and obesity, cardiovascular diseases, cancers and lung diseases, referred as chronic noncommunicable diseases, are the main causes of death related to increasing expectation of life. The mercury contamination can be causally associated with hyperglycemia by direct effect on pancreatic beta cells, with the pathogenesis of the metabolic syndrome, endocrine disorders, inflammatory diseases and the carcinogenic potential by oxidative stress. Metallic mercury compromises the lungs and kidneys, indirectly reflecting blood pressure, by inhalation. Hypertension can also be caused by methylmercury contamination, not only by renal impairment, but also mainly by the activation of the renin angiotensin system. Overweight and obesity are risk factors for cardiovascular events and may be correlated with systemic levels of methylmercury because of it lipophilic potential. These diseases represent a public health problem and affect the quality of life, life expectancy, treatment and hospitalization expenses, labor capacity and regional development. In this context, the epidemiological transition and nutritional transition should be evaluated as important covariates for understanding the effects of exposure to methylmercury on the health of the traditional populations in Amazon. Studies on the relationship between mercury and chronic noncommunicable diseases are extremely important and not enough explored in Amazonian risk populations. The present study aims to evaluate the possible relationship between methylmercury contamination and chronic noncommunicable diseases potentially related to this exposure factor in a riverine population of the Brazilian Amazon. The potential explanatory variables such as lifestyle habits, body-mass index, socioeconomic factors, hypercholesterolemia, selenium and n-3 fatty acid consumption were evaluated.

RP-083

ARE THERE CUMULATIVE TRENDS IN THE BIOACCUMULATION OF METHYLMERCURY DOWNSTREAM OF FOREST HARVESTING OPERATIONS IN NORTHERN HARDWOOD CATCHMENTS?

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As a global leader in the export of forest products, Canadian forest managers are tasked with balancing exploitation of one of the countrys most cherished natural resources with maintaining a high standard of forest ecosystem integrity. Despite environmental protection guidelines for forest management, legacies of ecosystem degradation persist, many of which are specific to aquatic environments. One example includes the accelerated input of atmospherically-deposited or weathered contaminants like mercury (Hg) into forest streams via terrestrial erosion following forest harvest operations. In aquatic environments, Hg is transformed by anaerobic bacteria at the sediment-water interface to methylmercury (MeHg), a neurotoxicant with high potential for bioaccumulation and biomagnification in aquatic food webs. In response to concerns for sustaining ecosystem integrity in the face of resource development, this study examines the impact of selection-based harvesting of northern hardwood stands in the Batchawana River watershed on the northeastern shore of Lake Superior in Ontario on bioaccumulation of MeHg in forest stream food webs. The study area consists of four catchments, each with three sampling sites of increasing stream order, that have been subject to either very little harvest (<15% area harvested) or substantial harvest (>60% area harvested) in the last 10 years. Bioaccumulation of methylmercury in northern hardwood stream food webs is assessed by measuring its concentration in stream water and in late instars of the larvae of ubiquitous filter-feeding caddisflies (Hydropsychidae) at all sites within these catchments. Other metrics of the impact of forest management on aquatic ecosystem health include water quality, leaf litter decomposition and associated macroinvertebrates, and fine sediment deposition. Ultimately, this study will look for evidence of whether or not bioaccumulation of MeHg and other impacts to stream health are spatially cumulative downstream of forestry activities, an analysis that has received relatively little attention despite its requirement under Canadian environmental assessment legislation. A comprehensive and predictive understanding of the spatially cumulative effects associated with forest management is critical to maintaining healthy future forests and provisioning of their aquatic ecosystem services.

RP-084

SPACE AND TEMPORAL DISTRIBUTION OF CONCENTRATION OF MERCURY IN ANTARCTIC FOOD WEB: A REVIEW

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Although more chemicals are reaching Antarctica, the link between those xenobiotics and specially mercury (Hg) exposure and its effects on Antarctic food web is still poorly understood. Antarctic organisms have long life cycles, tendency to gigantism and slow metabolic rates (due to low temperatures), being more inclined to accumulate and magnify Hg in its organic form methylmercury though the food web in comparison with species of lower latitudes. Due to the new global environmental problems, the study of Hg behavior in the Antarctic is urgent.

In order to identify the interaction of Antarctic species and Hg, a systematic study of the existing literature on the concentrations of these compounds in different organisms was conducted. The organisms considered were zooplankton, crustaceans, benthonic fauna, fish, seabirds and marine mammals. Some databases such as Direct, Springer, Scopus and Web of Science were used. Selection criteria corresponded to the levels of total Hg on the basis of dry weight (d.w.). Subsequently, this information was summarized in tables. Maps of the distribution of total Hg levels in different Antarctic locations were also considered, as well as Hg temporal distribution (80s, 90s and current time).

During the 80s, Hg average levels in crustaceans are < 0.1 µg/g, in seabirds 0.2 µg/g, while in marine mammals are 2.4 µg/g. During the 90s, Hg levels in crustaceans are 0.025 µg/g and in marine mammals 5.03 µg/g. More recently (between 2000-2016), Hg levels in zooplankton are 0.07 µg/g, in crustaceans 17.67 µg/g, in benthonic organisms 0.18 µg/g, in fish 0.36 µg/g, in seabirds 0.81 µg/g, and in marine mammals are 0. 2µg/g. According to metal distribution in Antarctic locations, the Hg levels are: Admiralty Bay > Antarctic Peninsula > Southern Ocean > Newfoundland Bay > Ross Sea > Bird Island > King George Island > Windmill Island > Antarctic Scotia Sea.

Mercury concentrations have been increasing over the years. More studies are needed in order to correlate reported levels with δ15N isotopes at different trophic levels. Likewise, more studies are needed in different Antarctic locations.

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RP-085

ECOLOGICAL FACTORS CONTROLLING INSECT-MEDIATED METHYLMERCURY FLUX FROM AQUATIC TO TERRESTRIAL ECOSYSTEMS: LESSONS LEARNED FROM EXPERIMENTAL STUDIES IN MESOCOSMS AND PONDS

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The diets of terrestrial consumers can be subsidized by energy and nutrients transported from aquatic ecosystems to terrestrial food webs by emergent aquatic insects. The cross-system transport of energy and nutrients by insects can have a dark side because emergent aquatic insects also transport toxic contaminants such as methyl mercury (MeHg) to terrestrial ecosystems when they emerge. Although many ecological factors influence insect emergence and the cross-system transport of energy and nutrients by insects, the ecological factors regulating insect-mediated MeHg flux have been little studied. In this presentation, we overview our mesocosm and pond experiments examining ecological factors regulating the transport of MeHg out of aquatic ecosystems by emergent insects. We calculate insect-mediated MeHg flux as the product of the MeHg concentrations and biomass of emergent insects. Ecological factors can impact insect-mediated MeHg flux either by affecting MeHg concentrations in emergent insects or by altering the biomass of emergent insects. We overview the effects of four ecological factors on aquatic insect-mediated MeHg flux: 1) predation and community structure, 2) nutrient limitation and productivity, 3) drying disturbance and pond permanence and 4) phenology of insect emergence.

RP-086

MERCURY CONTAMINATION IN BATS FROM THE CENTRAL UNITED STATES

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We surveyed mercury (Hg) concentrations in 10 species of bats collected at wind farms in the central United States and found contamination in all species. Mercury contamination in fur was highly variable both within and between species (range 1.08-10.52 μg/g). Despite the distance between sites (up to 1200 km), only 2 of the 5 species sampled at multiple locations had concentrations of Hg that differed between sites. The Hg concentrations observed in this study all fell within the previously reported ranges for bats collected from the northeastern United States and Canada, although many of the bats we sampled had lower maximum Hg concentrations. Juvenile bats had lower concentrations of Hg in fur than adult bats, and we found no significant effect of sex on Hg concentrations in fur. For a subset of 2 species, we also measured Hg concertation in muscle tissue; concentrations were much higher in fur than in muscle and Hg concentration in the 2 tissue types was weakly correlated. Abundant wind farms and ongoing post-construction fatality surveys offer an underutilized opportunity to obtain tissue samples that can be used to assess Hg contamination in bats.

RP-087

EFFECTS OF MERCURY DEPOSITION, FISH SPECIES AND FISH LENGTH CATEGORY ON MERCURY CONTAMINATION OF GAME FISH IN THE SOUTH CENTRAL UNITED STATES

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Because of its extreme toxicity and its widespread presence in aquatic food webs, methyl mercury (MeHg) poses a threat to human health. The primary pathway of MeHg into humans is through the consumption of MeHg-contaminated fish. Methyl mercury contamination of water bodies and their food webs vary across the landscape, and many ecological factors have been found to be correlated with MeHg contamination of fish. In this study, we examined the relationship between average MeHg concentrations in five fisheries length categories (stock, quality, preferred, memorable and trophy) of bluegill (Lepomis macrochirus) and largemouth bass (Micropterus salmoides) and average Hg deposition in 14 ecoregions located within all or part of six states in the south central U.S. We focused on bluegill and largemouth bass because they are widely distributed and economically important species of freshwater game fish. The National Descriptive Model of Mercury in Fish was utilized to estimate concentrations of MeHg in bluegill and largemouth bass. Mercury deposition was estimated using wet Hg deposition data from the Mercury Deposition Network adjusted for the presence of coniferous forests. Average MeHg concentrations of bluegill and largemouth bass increased with Hg deposition and fish length category. Only large length categories of bluegill in ecoregions with high levels of Hg deposition had average concentrations of total MeHg above 300 ng/g ww, the threshold concentration of MeHg recommended by the U.S. Environmental Protection Agency for the issuance of fish consumption advisories. The three largest length categories of largemouth bass had MeHg concentrations above 300 ng/g ww in all ecoregions. In ecoregions with high Hg deposition, the largest length category of bass (63 cm TL) had MeHg concentrations over four times greater than 300 ng/g ww. Our study suggests that in the south central U.S., atmospheric Hg deposition adjusted for the presence of coniferous forests sets the potential for MeHg contamination of fish, and that fish species and fish length category determine the observed levels of MeHg contamination. Over 90% of the ecoregion-level variance of MeHg concentrations in bluegill and largemouth bass was accounted for by Hg deposition adjusted for conifers, fish species and fish length category.

RP-088

BIOACCUMULATION OF MERCURY IN MUMMICHOGS (FUNDULUS HETEROCLITUS) AND ATLANTIC SILVERSIDES (MENIDIA MENIDIA) IN DUNN SOUND, SOUTH CAROLINA

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Two year round forage fish that reside in South Carolina salt marshes are mummichogs (Fundulus heteroclitus) and Atlantic silversides (Menidia menidia). Mummichogs target prey associated with Spartina alterniflora, from the sediment and within the water column while Atlantic silversides feed on zooplankton in the water column. This study quantified and compared levels of total and methyl mercury in mummichogs and Atlantic silversides from Dunn Sound, SC. Sample collection occurred in February, April, July, and October 2014, and an additional sample event occurred in April 2015 to obtain an annual comparison. Also, gut contents were quantified and compared to determine if there was a potential dietary impact on the concentrations of total and methyl mercury within these fish.

Atlantic silversides had significantly higher whole body total ($p < 0.01$, Two-Way ANOVA, Tukey) and methyl mercury ($p < 0.01$, Kruskal Wallace, Dunns Test) concentrations when compared to mummichogs for all of the sampling events. There was no significant difference between total ($p = 0.0683$, Two-Way ANOVA, Tukey) and methyl ($p = 0.1005$, Kruskal Wallace) mercury concentrations in the fish when comparing each sampling event. Although percent methylmercury in Atlantic silversides and mummichogs changed significantly by event ($p < 0.01$, Kruskal Wallace, Dunns Test) there was no significant difference between the species ($p < 0.3553$, Kruskal Wallace). This suggests that both species of fish assimilate mercury at the same rate.

When comparing April 2014 to April 2015, there was no significant difference in the total mercury concentrations between these fish ($p=0.3553$, Two way ANOVA). For both species, the concentration of methylmercury was significantly higher in April 2015 relative to April 2014 ($p<0.01$, Two- way ANOVA, Tukeys Test), however for both years Atlantic silversides had significantly higher methylmercury concentrations relative to mummichogs ($p<0.01$, Two- way ANOVA,

Tukeys Test). There was no significant difference between the percent methylmercury of both species (p=2919, Kruskal Wallace) but April 2015 had significantly greater percentages methylmercury than April 2014 ($p<0.01$, Kruskal Wallace, Dunns Test).

The quarterly percent gut contents by weight (%W) and number (%N) of Atlantic silversides were significantly different relative to mummichogs ($p < 0.01$, PERMANOVA). Atlantic silversides consumed greater numbers of crustaceans whereas mummichogs preyed on a variety of organisms within the food web. Differences in the mercury concentrations of these two fish may impact the bioaccumulation and biomagnification of mercury within the salt marsh food web.

RP-089

MERCURY BIOACCUMULATION ALONG FOOD WEBS IN FOUR TEMPERATE LAKES OF THE SOUTH WESTERN FRANCE (AQUITAINE REGION)

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Recently, in lakes of Aquitaine region, analysis conducted by ANSES (French Agency for Food, Environmental and Occupational Health and Safety) revealed total mercury concentrations (HgT) exceeding the International Marketing Level in muscle of zander (Sander lucioperca), a carnivorous fish, in 2 lakes (Carcans- Hourtin and Lacanau). A ban on consumption of this species was thus decided. Following this, a multidisciplinary research project was launched in order to better understand the biogeochemical cycle of mercury on these lakes and the origin of mercury.

This study focused on the four largest lakes of Aquitaine (Hourtin-Carcans, Lacanau, Cazaux-Sanguinet, Parentis-Biscarrosse), emblematic environments of the region, closely related to tourism. Each of these hydrosystems has its own characteristics (trophic levels, physicochemical factors, different anthropic pressure between the lakes ...). Their response to a contamination pressure and the evolution over time of this contamination will therefore be potentially different. This integrative study considers all the aquatic compartments: water, sediment, and different level of the trophic chain (phytoplancton, periphyton, macrophytes, mollusks, crustaceans and fishes).

The objectives of the first part of this project were: (1) to measure Hg concentrations in different compartments at one season (for fish: age assessed), (2) to study the structure of these food webs using nitrogen and carbon stable isotope analysis, (3) to check the mercury biomagnification along food webs and to identify a possible entry point of this pollutant in food webs.

The results indicate that carnivorous species like pike (Esox Lucius), zander (Sander lucioperca) and perch (Perca fluviatilis) may exceed the International Marketing Level depending on their size. A biomagnification of Hg along food webs was observed for lakes. A north-south mercury contamination gradient could also be highlighted: Hourtin-Carcans > Lacanau > Cazaux- Sanguinet > Parentis-Biscarosse. Several explanations concerning the origin of this gradient are now available but need to be further studied. This study provides information on the transfer of Hg in the lake ecosystems of south western France and makes it possible to evaluate the risk associated with the presence of Hg in aquatic food webs.

RP-090

IN VITRO BIOACCESSIBILITY OF MERCURY FROM TRADITIONAL FOODS OF BIGSTONE CREE FIRST NATION (ALBERTA, CANADA)

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Mercury (Hg) is a global pollutant of concern with impacts on public health and ecosystem quality. First Nations communities whose lives are heavily dependent on traditional foods are particularly susceptible to mercury exposure given that their traditional foods are known to be contaminated with mercury. Most studies have focused on mercury contamination in seafood consumed by First Nations communities, while relatively few studies have investigated other food types. Further, it is assumed that 100% of ingested Hg is bioavailable (reaches the systemic circulation) though new studies suggest that this may be less than 100%. The objective of this study is to characterize in vitro total mercury (THg) bioaccessibility from muscle tissue of four food items consumed by members of the Bigstone Cree Nation (Alberta, Canada).

The food items of concern (grouse, hare, fish, and duck) were collected through a participatory research activity. The THg levels in these samples ranged from 0.02 ppm to 0.34 ppm. Next, we will assess THg bioaccessibility using an in-vitro model of human digestion; bioaccessible THg will be measured in the soluble fraction of the digests. The expected results of this work are an increased understanding of THg bioaccessibility from a range of foods not previously studied, and ultimately improved abilities to assess exposure-related risks.

RP-091

SPATIAL DISTRIBUTION OF MERCURY LEVELS IN FLYING FISHES IN THE NORTHERN AND SOUTHERN HEMISPHERES

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Since the industrial revolution, atmospheric mercury (Hg) concentrations have been increased by anthropogenic emissions.

The Hg concentrations are higher in the Northern Hemisphere than the Southern Hemisphere because of a large extent of the industrial activities in the north. According to a global Hg model, the emitted Hg is likely transported and deposited within the same hemisphere. The deposited Hg can be converted to methylated form of Hg, which is neurotoxic and bioaccumulative in aquatic food webs. Pelagic fishes in the Northern Hemisphere are expected to contain more Hg than those in the Southern Hemisphere. The distribution of such an information has, however, been poorly obtained. In this study, total Hg (THg) and methyl-Hg (MeHg) concentrations in muscle of flying fishes from western Pacific and eastern Indian Oceans from 30° N to 41° S in latitude were measured. These samples can be used to evaluate the hemispheric and latitudinal Hg variations. The THg concentrations of the Northern Hemisphere flying fishes ranged from 30 to 450 ppb (d.w.), whereas the range in the Southern Hemisphere was between 50 and 530 ppb (d.w.). More than 90 % of Hg in most of the flying fishes were MeHg. There was no significant difference in THg concentrations between the Northern and Southern Hemispheres. Variations in THg concentrations of biota are often explained by different body length. Nevertheless, body lengths of the flying fishes in this study were poorly correlated. Positive correlations were observed between the THg concentrations of the flying fishes and latitude in the both Northern ($r = 0.42$, $N = 19$) and Southern ($r = 0.61$, $N = 8$) Hemispheres. The MeHg concentrations in the flying fishes were also positively correlated with the latitudes. It has been documented that MeHg concentrations of freshwater fishes are increased as wet atmospheric Hg deposition becomes greater. Therefore, the variations in Hg concentrations of the flying fishes likely reflect the magnitude of atmospheric Hg deposition. A global Hg model showed that Hg deposition fluxes were relatively large from 30° to 50° latitude in both hemispheres because of the global atmospheric circulation pattern and the distribution of industrialize areas within those latitudes. This study indicates that atmospheric Hg deposition is directly linked to the Hg levels in marine organisms.

RP-092

SPATIAL AND TEMPORAL VARIATION OF METHYLMERCURY CONCENTRATIONS OF ATLANTIC SILVERSIDES (MENIDIA MENIDIA) FROM LONG ISLAND SOUND

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Atlantic silverside (Menidia menidia) is an annual forage fish species whose populations reside in coastal embayments along the Atlantic Ocean. They substantially contribute to the diet of other predatory fish and are therefore a stepping-stone in the trophic transfer of contaminants to the higher trophic levels. Atlantic silversides also serve as a model for planktivorous marine fish in studies of contaminant bioaccumulation, including total mercury (THg) and methylmercury (MeHg). We therefore investigated the spatial and seasonal variability of THg and MeHg in the pelagic food webs of five Long Island Sound (LIS) embayments. Seawater, the suspended particles, copepods, and fish were collected in May, June, July, and September of 2016 from these embayments from Norwalk Harbor in the Western part of LIS to Mumford Cove in the East. Suspended in seawater particles were collected via 20 µm and 3 µm pore size filter membranes to capture the particle pool most relevant to copepod diet (i.e. 3-20 µm). Female copepods of the same species and of similar size were "hand-picked" under the dissecting microscope to limit data variability. Presently no data is available on intersex and interspecies MeHg concentration differences in LIS copepods. Adult fish but not the juveniles were separated based on sex. Muscle tissue was dissected from the adults but for the juvenile fish head and fins were cut off and the abdomen was used for the analysis. Our results show an increase of MeHg concentrations in the silversides from both Mumford Cove or Norwalk Harbor from May to July, but MeHg concentrations in fish from the intermediate locations remained similar during that period. Overall, adult female silverside had MeHg concentrations of 0.34 ± 0.14 (mean ± SD) µg/g dry weight that were 18% higher than males. MeHg concentrations in 2-3 month old silverside juveniles were 0.13 ± 0.05 µg/g dry weight. MeHg concentrations in the copepods were highest in Mumford Cove and decreased towards the Western Sound. Highest MeHg concentrations in copepods from Mumford Cove were found during May and June and declined by 50% in July. The east-west gradient of MeHg concentrations in copepods was steepest in May and least pronounced in July. Insufficient copepods were found in September, likely due the bloom of their predators, gelatinous zooplankton. We will present the bioaccumulation and trophic transfer trends in studied LIS embayments during the spring and summer of 2016.

RP-093

TOTAL MERCURY CONCENTRATION IN JAGUAR (PANTHERA ONCA), TAIAMÃ ECOLOGICAL STATION, PANTANAL OF MATO GROSSO, BRAZIL

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Mercury is one of the pollutants most resistant to degradation and its bioaccumulation can be highly harmful to aquatic biota, transposing trophic chain levels and reaching top food chain predatory mammals. The Taiamã Ecological Station is a Federal / ICMBIO reserve. The jaguars of Taiamã have as preferential diet the fish and alligator, already evaluated in other studies as bioindicators of mercurial contamination in the Pantanal of Mato Grosso, Brazil. The objective of this study was to evaluate the concentrations of total mercury in jaguar (Panthera onca), using a non - invasive method of barbed wire and adhesive tape and collection of hairs samples obtained in collar / ICMBIO / CENAP. For the composite samples, seven sample points were monitored for six months with a Trap camera, with the objective of individualizing them. A total of 15 samples were collected, of which 13 were individual and 02 were composites (03 and 04 individuals per sample). For the quantification of the concentrations of total mercury was used atomic absorption spectrophotometer, Perkin Elmer (FIMS - system). The average concentration of mercury (µg.Kg) was 4,265,448 (2,130,531 min and 7,259,444 max). There was no significant difference in the concentrations of total mercury between the sexes (T test = 1,571, df = 10.8, p = 0.143), although the females presented the highest concentrations, which surely can cause over the years to Biodiversity. Age also did not explain the variations in concentrations (R2 = 0.1603, p = 0.1753). However, there was a significant negative difference between the concentrations of total mercury and the animals' weight (R2 = 0.3516; p = 0.03269). Thus, lighter animals had the highest concentrations of mercury in the body, suggesting that a mercury demethylation mechanism may be occurring over the life of these animals or individual factors of metal absorption in the body. The results are unprecedented and demonstrate bioaccumulation through trophic chain levels, reaching the largest predatory cat in the Pantanal, Mato Grosso, Brazil through its diet almost exclusively of fish and alligators.

RP-094

ORGANOTROPISM OF MERCURY IN TWO CARNIVOROUS FISHES SPECIES FROM THE AMAZON REGION, BRAZIL

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The Amazon region is considereda region with natural mercury (Hg) in soils.However, since the 1980s, tons of Hg were released from the gold mining activity. This fact raises ecological concerns, due this chemical element undergobiomagnification along the trophic chain, reaching the human beings. Thus, fish as the main vectors of methylmercury (MeHg) for human population in the Amazon, demand studies that understand the Hg dynamics in its organisms. The aim of this study was to evaluate the organotropism of Hg in fish tissues (muscle, liver, gills and brain) of the carnivorous species Cichlamonoculus and Pseudoplatystomafasciatum, sampled in Puruzinho lake (Madeira river, Amazon state).These species are consideredas chain top organisms due shows carnivorous food habit. In addition,such species are widely consumed by the riverine population. Fish samples were obtained by fishing net from August 2014 to July 2015. A chemical solubilization (HNO3: H2SO4) was performed for the total mercury determination (THg), followed by oxidation (KMnO4at 5%) and a pre-reduction (NH2OH. HCl at 12%) for further quantification in a cold vapor atomic absorption spectrophotometer.Extraction of methylmercury (MeHg)was carried out through a basic solubilization (KOH at 25%) keeping the sample in an oven at 70°C for 6 hours. Subsequently, aliquots of fish tissue samples were transferred into the vials and buffered with 2M of NaC2H3O2. The samples were ethylated by the addition of NaBEt4 and measured with ultra-pure water for further determination in a gas chromatograph coupled atomic fluorescence spectrophotometer. The analytical quality control was done using certified reference muscle samples (DORM-2 - dogfish).The mean of THg concentrations inP. fasciatum followed the order Liver >Muscle>Brain>Gills, showing a similar order for MeHg in C. monoculus. The order of concentration for THg was Liver>Muscle>Brain>Gills. For the concentrations of MeHg the species followed the same pattern as the first.Percentage of ratio (MeHg/HgT) of the species P. fasciatum was Gills>Brain>Muscle>Liver, and for C. monoculus was Gills>Muscle>Brain>Liver. The highest concentrations of HgT are present in the muscle and liver of the species P. fasciatum and C. monoculus respectively, and thus the highest organotropic ratio of HgT in these species due to their carnivorous food habit.

RP-095

VARIABILITY OF MERCURY CONCENTRATIONS IN LAKE STURGEON FROM FIVE RIVER SYSTEMS IN MANITOBA, CANADA

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In 2006, the Committee on the Status of Endangered Species in Canada (COSEWIC) assessed most Lake Sturgeon (Acipenser fulvescens) populations in Manitoba as endangered, although they have yet to be formally listed under the Federal Species at Risk Act (SARA). Currently, commercial and recreational harvest is entirely prohibited, but varying degrees of subsistence harvest persists throughout much of the province. For many First Nation communities in Manitoba, Lake Sturgeon is an important traditional food source and is generally considered an essential and integral part of their distinct cultural identity. Community members occasionally consume large quantities of sturgeon and concerns have been expressed about the associated health risk from mercury exposure. Sturgeon are long-lived, regularly feed on large invertebrates and fish, and thus may accumulate mercury at substantial rates over several decades. However, relatively little is known about mercury concentrations in Lake Sturgeon in Manitoba (and elsewhere in North America). Over the past decade, incidental sturgeon mortalities from several environmental monitoring programs and other environmental assessments in Manitoba have been sampled and analyzed for total mercury (THg) in the axial musculature, substantially expanding the existing data base. Here, we summarize THg concentrations for almost 300 Lake Sturgeon collected from 10 river reaches located within five river systems (four regulated, one unregulated) throughout Manitoba. Mercury concentrations in sturgeon measuring between 97 and 1390 mm fork length and age O+ to 51 years ranged from 0.01 ppm to 0.67 ppm. Mean and median concentrations were 0.12 ppm and 0.09 ppm, respectively, and mean and median lengths were 684 mm and 664 mm, respectively. Except for those from the Saskatchewan River, sturgeon from all other rivers showed a significant relationship between THg and fish length. The slope of the THg-length regression significantly differed between some sturgeon populations, indicating differences in their rate of mercury bioaccumulation. The few available fish from the unregulated Hayes River had the steepest slope of all populations. Thirty (12%) sturgeon exceeded a mercury concentration of 0.2 ppm, which is generally considered the limit for unrestricted fish consumption for subsistence purposes by health organizations. These 30 sturgeon had a mean length of 1053 mm, indicating that subsistence harvest should avoid larger fish to reduce dietary mercury exposure.

RP-097

RELATIVE IMPORTANCE OF TISSUE GROWTH RATE ON HG AND PCB DYNAMICS IN FISH

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This study evaluated the effect of growth of different tissue compartments on the bioaccumulation of mercury (Hg) and polychlorinated biphenyls (PCBs) in silver carp (Hypophthalmichthys molitrix) and bighead carp (Hypophthalmichthys nobilis) from the Three Gorges Reservoir (TGR), China. It was observed that although Hg increased with fish age and size in both species, there was little evidence of PCB concentrations being related to fish size. To investigate this anomalous pattern of bioaccumulation, model simulations were developed and revealed that the growth rate coefficient (kg) of storage tissue compartments exceeded whole body elimination coefficients (ktot) of each contaminant. The kg of lipids also exceeded the kgof protein when expressed on a per unit tissue basis. Using the actual tissue specific kgand calibrated Cd(PCB or Hg concentration in diet), a general bioaccumulation model was able to accurately predict bioaccumulation of PCB and Hg in these two species and major inflection points of chemical accumulation. This study concludes that kgis a dominant process regulating the bioaccumulation of Hg and PCB in silver and bighead carp populations of the TGR. Furthermore, the wider fluctuation in kgof lipid than kg of protein can lead to higher variability in the PCB bioaccumulation rate compared to Hg.

RP-098

ASSESSMENT OF MERCURY CONTAMINATION IN RIVERINE FISH ASSOCIATED WITH UNCONTROLLED GOLD MINING IN MADRE DE DIOS, PERU

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Artisanal and small-scale gold mining (ASGM) in the Madre de Dios region of Peru is causing widespread environmental damage. As global market prices of gold increase, the rainforest is rapidly being cleared for alluvial mining. More than 100,000 acres of protected rainforest have been destroyed by illegal mining over the past decade. As hillsides are washed away, miners use elemental mercury to recover gold in a rudimentary amalgamation process, which is likely driving significant mercury contamination downstream.

The objective of this study is to assess the level of environmental contamination of recent ASGM activities in Madre de Dios. We will monitor sites in the Tambopata and Heath Rivers. Tambopata River receives inputs from the mining-impacted Malinowski River. The Heath River watershed remains undisturbed. Both rivers are in the Tambopata National Reserve and have similar watershed characteristics, such that under normal conditions they would be expected to have similar water quality and ecological conditions.

Samples will be collected at four sites during the rainy season (January-March) and dry season (July-September) in 2017. Sampling sites are in the Tambopata River (one each upstream and downstream of the Malinowski River tributary), one in the Malinowski River, and one in the Heath River. We will quantify the concentrations of mercury (total and methyl mercury) in fine-grained riverbed sediments and in four sentinel fish species (Donsello, Boca chico, Chambira, and Paco). Ancillary physical and chemical parameters (temperature, turbidity, pH, dissolved oxygen, and nitrate) will be measured in-situ. Results from the rainy season will be presented and discussed. We expect to identify distinct patterns between the two river ecosystems and to use the Heath Rivers data as a baseline for future monitoring.

RP-099

MERCURY ASSESSMENT AS PART OF THE CALIFORNIA STREAM QUALITY ASSESSMENT

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As part of the U.S. Geological Survey (USGS) Regional Stream Quality Assessment studies; the California Stream Quality Assessment (CSQA) evaluated mercury in water, sediment, and fish at 85 stream sites in the coastal chaparral ecological region during spring 2017. The study region spans ~520 km from Santa Barbara in the south to Santa Rosa area in the north and is home to roughly 8 million people as well as is a major agricultural setting that provides much of the nations produce. There are numerous potential sources for mercury (Hg) and other trace elements in the CSQA region, such as selenium that may impact mercury occurrence and bioaccumulation. Sources for Hg include industrial wastewater, municipal wastewater, urban storm runoff, natural geothermal sources, mercury mines, gold mines, and direct atmospheric deposition. The number of mercury mines in the upstream watersheds of the sampling sites ranges from 0 to as many as 50 mines. Many of the watersheds within this region have total maximum daily load limit (TMDLs) management plans in place for mercury. CSQA sampling included weekly water chemistry for six weeks culminating in sampling of bed sediment and full ecological surveys at each site. Fish tissue samples were collected at most sites for analysis of total mercury in composite samples of insectivorous forage fish. Opportunistically game fish were collected and analyzed for total mercury in the fillet tissue. Carbon and nitrogen isotopes were used to evaluate tropic position of the fish. Mercury isotopes were assessed in bed sediment and fish tissue at selected sites to evaluate potential sources of mercury. In addition, water quality information was collected (e.g., dissolved organic carbon, sulfate) that might help to explain mercury methylation in the streams and concentrations of Hg in fish. These results will aid in better understanding the conditions of these streams within this region and assist future management of these streams and downstream waterbodies.

RP-100

CHARISMATIC MINI-FAUNA CONNECT CITIZEN SCIENTISTS TO MERCURY AIR AND WATER POLLUTION ISSUES IN NATIONAL PARKS: THE DRAGONFLY MERCURY PROJECT

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The Dragonfly Mercury Project engages citizen scientists in monitoring mercury contamination in National Parks across the US. The scientist team at the University of Maine, US Geological Survey, and National Park Service (NPS) enlist park staff or community partners, who lead teams of citizen scientists in the collection of dragonfly larvae. Dragonflies are analyzed for mercury, a global pollutant that affects resources the NPS is charged with protecting. The results provide individual parks and NPS data regarding the distribution of mercury at broad spatial scales. Our goals for citizen scientist engagement are to: (1) provide an opportunity for biodiversity discovery; (2) connect people to parks; and (3) provide a vehicle for education and outreach regarding mercury. After field sampling, each park lead completes a short phone survey to provide structured feedback about citizen scientist outcomes. Since 2013, we have conducted a consistent survey covering >100 sampling expeditions across 60 national parks, involving >2,500 citizen scientists who typically contribute ~4 hours each to the project. Preliminary results indicate that deep engagement in the biodiversity discovery objective was an overwhelmingly important aspect of the project, with several participants citing getting kids outdoors as a highlight of the program. At Acadia National Park, expanded sampling plans allowed for multiple citizen science expeditions, with over 660 participants (from middle school students to families to retirees) during 2013-2016. We will discuss our development of key messages for each citizen group type and outline challenges of working with the various citizen groups.

RP-101

MERCURY IN STREAM ECOSYSTEMS OF THE CHESAPEAKE BAY COASTAL PLAIN: USING INVERTEBRATES TO EVALUATE FOOD WEB EXPOSURE

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Methylmercury (MeHg) is produced in numerous aquatic ecosystems. Some systems have the potential to easily transfer and biomagnify into both aquatic and terrestrial food webs. While bioaccumulation processes within higher trophic levels have been well documented, processes controlling methylation of inorganic mercury (Hg) and initial steps of accumulation of MeHg into the food web are not as well understood. We have been studying mercury cycling in stream ecosystems at the Smithsonian Environmental Research Center (SERC) which is located on the Coastal Plain on the western shore of the Chesapeake Bay. One part of this research is focused on the transfer of MeHg and Hg to the food web of two first order streams with different watershed histories, one which has been forested for the past 80 years and one that until recently supported agriculture. Production of MeHg in the riparian zone occurs in both streams, but stream and shallow groundwater concentration are much higher in the forested stream. By measuring concentrations of MeHg in sediment, stream pore water, and benthic macroinvertebrates of the two stream ecosystems, we are attempting to identify benthic macroinvertebrate taxa to serve as bioindicators in MeHg risk assessment. Initial examination of macroinvertebrate species diversity and abundance indicates an anticipated difference between the two watersheds, but with some commonality to explore our question. This difference is likely driven by the differing hydrology between the forested and the agriculturally impacted watershed. MeHg and Hg analysis is currently underway and the results will be presented.

RP-103

ENVIRONMENTAL SELENIUM IS INVERSELY RELATED TO MERCURY BIOACCUMULATION IN FRESHWATER FISH

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A recent study that assessed the mercury (Hg) and selenium (Se) concentrations in >14,000 ocean and freshwater fish has found the overwhelming majority of ocean fish contain far more Se than Hg, and are therefore more likely to prevent than cause Hg toxicity. In contrast, the Hg contents of freshwater fish are inversely related to environmental Se availability, introducing great variability in the risks associated with their consumption. For this reason, the effects of methylmercury (MeHg) exposures from fresh water fish consumption require a better informed approach to risk assessments than those previously available. In all vertebrate tissues, MeHg initially binds to thiols, but since substrate thiols are directly acted upon by certain selenoenzymes, these species become suicide substrates that actively deliver MeHg into the active sites of Se-dependent enzymes in the proper orientation to accomplish its transfer from the substrate thiol to the enzyme selenol. These MeHg-Se conjugates degrade to form mercury selenide (HgSe), an insoluble, biologically unavailable form that cannot be absorbed during digestion. This retires Hg from the biogeochemical cycle, and diminishes the amount available in tissues of predators or human consumers. Because the soils of many North American watersheds are Se-rich, fresh water fish from most regions contain far more Se than MeHg. However, fish from certain regions of North American and many other regions of the world have poor Se availability, either due to low abundance in the geological parent rock material, or due to poor Se bioavailability due to low pH of the watersheds soil or waters. Poor Se availability in freshwater bodies was found to greatly increase MeHg bioaccumulation in Lepomis machrochiris (bluegill), Sander vitreus (walleye), Ictalurus punctatus (channel catfish), Esox Lucius (northern pike), and Micropterus salmoides (largemouth bass). In the absence of sufficient Se, freshwater fish bioaccumulate more MeHg than fish from Se-rich watersheds, and their poor Se contents greatly increase the risks associated with these MeHg exposures. Therefore, these aspects of MeHg associated risks urgently require further study, especially in regions of the world which are known to be Se-poor. The risks associated with eating fish from such watersheds will need to be established on a case by case basis. In summary, MeHg risks cannot be accurately evaluated using outdated methods that only consider MeHg exposures. The Se-Health Benefit Values (HBV) is intended to enable rapid identification of areas at accentuated risk and will more accurately establish MeHg-exposure related health hazards.

RP-104

TEMPORAL TRENDS OF ZOOPLANKTON METHYLMERCURY CONCENTRATIONS IN THE FINGER LAKES, NEW YORK

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Zooplankton are an important vector of methylmercury (MeHg) to aquatic food webs and can be used to assess the role of morphological, land cover, and water quality parameters on MeHg availability. The Finger Lakes (New York, USA) are a series of glacially formed lakes with land cover dominated by agriculture that are experiencing increasing eutrophication. The objective of this study was to evaluate the association of lake productivity, frequency of anoxia, and dissolved organic carbon concentrations with temporal trends in zooplankton MeHg concentrations. Lakes were selected with contrasting land use, watershed size, and depths. We surveyed bulk zooplankton (153 m mesh size) weekly from Honeoye Lake and Seneca Lake in May September 2016. Honeoye Lake is a shallow (max depth 9 m), polymictic lake that undergoes frequent anoxia over the summer while Seneca Lake is a deep (max depth of 198 m), monomictic lake that remains oxygenated in the hypolimnion. We hypothesized that Honeoye Lake will have higher MeHg concentrations in zooplankton due to the frequent anoxic events which can lead to higher MeHg production, and the greater catchment area to surface area ratio (CA:SA) which can increase Hg transport from the watershed. In a preliminary subset of samples, MeHg concentrations were low in both lakes (range = 2 21 ng/g dry weight (dw); mean 10 ng/g dw) compared to bulk zooplankton of a similar size class from other regional watershed systems including Lake Champlain and the Adirondacks. Zooplankton data collected monthly (May-September) in 2015 from a previous study of five Finger Lakes showed significant differences among lakes in May, July, and September. Within lakes, trends varied, but lakes with larger CA:SA (e.g., Honeoye Lake) had significantly higher MeHg concentrations in May. Dissolved organic carbon was not a significant predictor of zooplankton MeHg concentrations with the monthly samples collected in 2015. Analyses of the 2016 zooplankton samples continue and we hypothesize that changes in zooplankton MeHg concentrations on a finer temporal scale will reveal higher MeHg concentrations in Honeoye Lake compared to Seneca Lake.

RP-105

MERCURY IN FISH AND INVERTEBRATES IN THE SAINT JOHN RIVER ESTUARY

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Although methylmercury (MeHg) can be higher in freshwater than estuarine or marine sediments, it is not known whether MeHg in biota also follows this trend. The objective of this research was to determine if MeHg concentrations in fish and invertebrates decrease along gradients of increasing marine influence in estuaries, as measured by salinity. Fourspine stickleback (Apeltes quadracus), as well as invertebrates (snails, amphipods and chironomids), were collected from each of ten sites along the Saint John River estuary in 2015 and 2016. Sediments and water were also collected in 2016. Total mercury (THg; used as a proxy for MeHg in fish) was measured in whole stickleback and MeHg was measured in pooled invertebrates as well as sediments and water. Stable sulfur (δ34S) (measure of marine influence), carbon (δ 13C) (measures of food sources) and nitrogen isotope (δ 15N) (measure of trophic position) values were also measured, as these help explain variability in MeHg and THg in animals. Analysis of variance tests were used to check for among-site differences in THg in fish and generalized linear models were used to determine which factors predict THg in stickleback and which factors (salinity, dissolved oxygen, length (fish only) and stable isotope values) predict MeHg in invertebrates. Salinity and dissolved oxygen of the sites ranged from 0.1 ppt to 8.1 ppt and from 5.9 to 12.2 mg/L, respectively. Concentrations of THg in stickleback were 109.4 to 1,134.1 µg/kg dry weight (dw) across sites. MeHg ranged from 10.1 to 145.1 µg/kg dw in amphipods, from 22.1 to 613.0 µg/kg dw in snails and from 23.4 – 101.0 µg/kg dw in chironomids across sites. Though there were significant among site differences in THg in fish, these differences seemed to be unrelated to salinity. For stickleback in 2015, mean THg was best predicted by mean length and δ34S. MeHg in both amphipods and snails were significantly predicted by d15N. Although several factors affect the accumulation of MeHg in the tissues of biota, these preliminary results do not suggest salinity was a main influence, although δ34S, another measure of marine influence, explained some variability of THg in 2015 fish. Analyses of samples and data from 2016 is ongoing.

RP-106

A REGIONAL INVESTIGATION OF MERCURY IN SMALL MID-TROPHIC FISHES AND PREDATORY GAME FISHES OF STREAMS IN THE NORTHEASTERN UNITED STATES

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Fish-tissue mercury (Hg) concentrations exceed human health advisory levels and wildlife guidelines in water bodies throughout the northeastern United States. Mercury concentrations in small, mid-trophic level invertivorous fishes and in predatory game fishes of this regions streams were assessed during the summer of 2016 as part of the Northeast Stream Quality Assessment (NESQA), a multi-stressor study conducted by the USGS National Water-Quality Program. The objectives of the fish mercury investigation were to document stream-fish Hg concentrations throughout the region and to describe the environmental factors associated with observed spatial patterns across the region. Streams were located in urban, agricultural, and forested watersheds, and represented a variety of potential mercury sourcess. Total mercury (THg), assumed to be primarily methylmercury (MeHg), was analyzed in fish tissue collected from 91 streams. Small-bodied, mid-trophic, invertivorous fishes were collected from nearly every site, and game fish samples were collected from 54 of the sites. Fish tissue from 23 of the sites was also analyzed for THg isotopes to evaluate Hg sources. The most commonly-collected mid-trophic level fishes were Blacknose Dace (*Rhinichthys atratulus*, 61 sites), Longnose Dace (*R. cataractae*, 22 sites), and Creek Chub (*Semotilus atromaculatus*, 22 sites). These samples consisted of single-species composites of whole specimens. The most commonly-collected game fish samples were salmonids (collected from 26 sites) and centrarchids (mainly *Micropterus* and *Lepomis* species; collected from 21 sites). Multiple mid-trophic level species and game fish species were collected at many sites, to facilitate spatial comparisons across the region. Fish and periphyton samples also were analyzed for nitrogen stable isotopes (δ15N) to provide estimates of base-adjusted trophic position (i.e. by adjusting fish δ15N for differences among sites in base nitrogen signature). Fish Hg concentrations will be compared with human-health and wildlife-health guideline levels, and will be analyzed in relation to stream physical data (such as stage, temperature), water quality data (including pH and concentrations of dissolved organic carbon, sulfate, THg and MeHg), bed sediment THg, landscape characteristics, and food web characteristics (based on periphyton, macroinvertebrate, and fish community sampling data) to document factors affecting mercury bioaccumulation in stream-resident fish across the Northeastern United States.

RP-107

MULTI-PREDATOR PROJECT: AN ANALYSIS OF TROPHIC ECOLOGY AND MERCURY BIOACCUMULATION BY CO-HABITING PISCIVORES

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Fish mercury (Hg) concentrations are positively correlated to atmospheric deposition. While North American and global deposition of Hg has declined in recent decades fish Hg concentrations in Boreal Shield lakes of Ontario, Canada, have not shown a similar decline and may even be rising in some areas. At a landscape scale, much of the observed variability in fish Hg concentrations is among waterbodies suggesting ecosystem-level effects on methylmercury production. There is also considerable variation among trophic guilds of fishes within waterbodies, with piscivores usually having the highest Hg concentrations. Variation in Hg concentrations may also be substantial among species within a trophic guild, though the reasons for this have not been closely investigated. We are examining the relative roles of food web position and growth rate in accounting for interspecific variation in mercury concentration of four co-habiting native piscivore species (walleye, northern pike, lake trout and burbot) in 34 Boreal Shield lakes of Ontario. Preliminary results have shown that variation among lakes may be higher than variation among species and much of the interspecific variation in mercury concentrations among boreal piscivores may be accounted for by subtle differences in food web position. Hg and stable isotope data analyses are ongoing, linear models relating total mercury concentration [THg] to carbon source (inferred from 13C), trophic position (inferred from 15N) and growth rate in a standard size of fish (1 kg) will be compared using Akaikes Information Criterion (AIC).

RP-108

MODELING MERCURY BIOACCUMULATION IN THE MICROBIAL FOOD WEB

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Methylmercury (MeHg) bioaccumulates in food webs. The length of microbial food webs differs between heterotrophic and autotrophic dominated systems. This difference in length could affect the level of MeHg bioaccumulation between the water column and zooplankton communities. Biogeochemical models often have a reduced pelagic microbial food web with simplified carbon and nutrient turnover. To quantify the uptake and trophic transfer of MeHg through the bottom of the food web we use the Baltsem model, a biogeochemical model that has been expanded to include a microbial food web. The model thus includes a detailed scheme for carbon and nutrient cycling in the water column and through three types of phytoplankton (cyanobacteria, diatoms and flagellates), bacteria, heterotroph nanoflagellates, ciliates and mesozooplankton. We recently updated the model to include biogeochemical Hg cycling in the water column and uptake into phytoplankton. Here we add uptake by bacteria as well as trophic transfer of MeHg through both the autotrophic and heterotrophic food web up to mesozooplankton. To validate the model we collected different size classes of seston in the Baltic Sea. The microbial communities in the samples were determined as well as the MeHg content. With the updated model we simulate differences in trophic MeHg transfer between the autotroph and heterotroph food webs. We discuss results from the model simulations with a focus on the impact of variability in autotroph/heterotroph driven food webs for MeHg bioaccumulation.

RP-109

ROLE OF MICROPLANKTONIC SPECIES IN MERCURY BIOACCUMULATION IN THE PELAGIC FOODWEB OF AN ULTRAOLIGOTROPHIC LAKE

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In ultraoligotrophic lakes of Andean-Patagonia, the aquatic biota generally bears high total mercury (Hg) levels. In these systems, inorganic Hg (Hg2+) makes up to ~93% of the Hg pool. The microplanktonic fraction (20-200 m) of these lakes is dominated by autotrophic dinoflagellates, (Gymnodinium spp.) and mixotrophic ciliates (Ophrydium naumanni and Stentor araucanus). These organisms may potentially incorporate Hg passively from the dissolved phase and, in the case of the mixotrophic ciliates, also through consumption of picoplanktonic organisms, transferring this metal to higher trophic levels. In this investigation we analyzed the passive and active incorporation of Hg2+ by three basal planktonic organisms of contrasting sizes (increasing size: Gymnodinium spp.

RP-110

TEMPORAL FISH MERCURY TRENDS IN RELATION TO FOOD WEB DYNAMICS IN LITTLE MOOSE LAKE, ADIRONDACKS NY

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Mercury contamination within aquatic ecosystems is of particular concern in the Adirondack Park of New York State due to elevated levels of mercury deposition from global and regional atmospheric sources and watershed characteristics that drive biophysical interactions that mobilize and transform mercury altering its bioavailability. Short-term internal biological forces impact mercury bioaccumulation as fish communities and populations change due to species introductions and lake management practices causing alterations in food web structure and energy transfer. Utilizing archived samples and historical data, total mercury concentrations, diet and age data were evaluated for lake trout, the native top-predator, and smallmouth bass, an introduced top-predator removed annually for over 15 years from Little Moose Lake in the Adirondacks. Mercury concentrations in lake trout have increased over time while smallmouth bass mercury concentrations decreased significantly over the same interval and so changes in mercury deposition are likely not the main driver for these observations. Diets for both species also changed over time with lake trout consuming higher trophic level prey containing higher levels of mercury. The annual bass removal could result in shifts in many different trophic transfer mechanisms that may have influenced the observations in temporal mercury trends in the two top-predator species. The knowledge gained from this in-depth study will allow better evaluation and monitoring of spatial patterns and temporal trends in sportfish mercury concentrations in the context of food web changes to protect human health and the environment.

RP-111

USING CYSTEINE TO QUANTIFY THE BIOMAGNIFICATION OF METHYLMERCURY IN AQUATIC FOOD WEBS: A NOVEL APPROACH

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The average biomagnification of methylmercury (MeHg) through aquatic food webs is quantified as the slope of log MeHg versus stable nitrogen isotopes (delta15N; a measure of relative trophic position). However, these slopes can vary significantly among ecosystems for reasons that are not well understood. In biota, MeHg is stored in proteins, in particular it is bound to the sulphur-containing amino acid cysteine. Our hypothesis was that cysteine content is a better and more consistent predictor of MeHg transfer through lake food webs than delta15N. In 2013, food web taxa (benthic invertebrates, zooplankton, and fish) were collected from six lakes within Kejimkujik National Park, Nova Scotia, Canada, a biological MeHg hotspot. MeHg concentrations and delta15N were measured and compared to protein-bound cysteine (measured as cysteic acid using ultra performance liquid chromatography) in composite invertebrate samples and fish muscle. Cysteine content (nmol per mg tissue) had a strong positive correlation with delta15N (Pearson correlation, $r = 0.86$; $p < 0.001$). In addition, log MeHg (mg/kg dw) was significantly and positively related to log cysteine (nmol per mg total protein) ($r2 = 0.74$-0.90; $p < 0.001$) within food webs across all lakes; no among-system differences in these slopes were observed (ANCOVA interaction term, $p = 0.2134$). For these same systems, relationships between MeHg and delta15N resulted in a better goodness of fit ($r2 = 0.90$-0.95; $p < 0.001$) and similar slopes (ANCOVA interaction term, $p = 0.5059$). These results suggest that while cysteine content was a significant predictor of MeHg in aquatic food webs, delta15N explained more of the among-taxa variability within each system.

RP-112

BOTH TROPHIC AND BIOGEOCHEMICAL PROCESSES CONTRIBUTE TO HABITAT-SPECIFIC MERCURY BIOACCUMULATION

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Bioaccumulation of mercury in fishes is often a complex process influenced by numerous biogeochemical, ecological, and physiological factors at various hierarchical levels. Habitat-specific foraging, including specialization on either littoral or pelagic resources, can be a particularly important ecological process influencing fish tissue mercury concentrations. However, the mechanisms underlying habitat-specific differences in mercury bioaccumulation are poorly understood. In particular, the degree to which differences in mercury bioaccumulation among habitats are due to trophic processes occurring within habitat-specific food webs as compared to variable production of bioavailable methylmercury in different habitats is unclear. To differentiate between these two sources of variation, we measured total mercury and methylmercury concentrations in threespine stickleback fish (Gasterosteus aculeatus) and primary consumers from both littoral (grazing snails) and pelagic (filter-feeding mussels) food webs in seven lakes where the proportion of the lake that was composed of littoral habitat ranged from 10% to 99%. Preliminary results indicate that in all seven lakes methylmercury concentrations of primary consumers were significantly (2- to 4-fold) higher in pelagic taxa than in littoral taxa. However, MeHg concentrations in primary consumers from both habitats displayed nearly identical positive correlations with the proportion of littoral area within lakes. In contrast, we found an inverse-quadratic (U-shaped) relationship between stickleback mercury concentrations and the proportion of littoral area within a lake; concentrations were higher in lakes with proportionally low or high littoral area compared to lakes with nearly equal proportions of the two habitats. Higher mercury concentrations in stickleback from lakes with high relative littoral areas may be due to higher mercury concentrations in the primary consumers at the base of these lakes food webs. However, lakes with low relative littoral area also had low mercury concentrations in primary consumers, suggesting that the elevated concentrations in the stickleback from these lakes are likely due to trophic processes occurring within the food webs. Together these data highlight the importance of considering both trophic and biogeochemical processes when evaluating habitat-specific sources of variation in mercury bioaccumulation.

RP-113

MERCURY BIOACCUMULATION, FATTY ACID PROFILES, AND STABLE ISOTOPES IN SWEDISH AND CHINESE LAKE FOOD WEBS

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The consumption of fish is the major exposure route of potentially toxic mercury (Hg) as well as physiologically highly required long-chain polyunsaturated fatty acids (PUFA) to humans. There are considerable differences in Hg and PUFA concentrations of freshwater fish in Sweden and China, with generally lower methyl mercury (MeHg) concentrations in fish from China than Sweden, although aqueous MeHg concentrations are very similar. Such inconsistence encouraged us to explore Hg, MeHg, and PUFA patterns in lake food webs to better understand the contrasts between the freshwater ecosystems of Sweden and China, as well as the large variation within each country. To do this we measured Hg and MeHg concentrations in surface water, plankton, benthic invertebrates, and fishes sampled from 7 freshwater lakes in Sweden and 6 reservoirs in China. Stable carbon (d13C) and nitrogen (d15N) isotope ratios, and PUFA concentrations

were measured in aquatic biota. We also included MeHg concentrations and PUFA profiles in different plankton size groups: seston (<25 µm in Sweden), microplankton (64-112 µm in China; 25-100 µm in Sweden), mesozooplankton (112-500 µm in China; 100-500 µm in Sweden) and macrozooplankton (>500 µm in Sweden).

Our preliminary results indicate: 1. Chinese fish muscle samples were rich in the omega-6 PUFA linoleic acid (LIN), whereas Swedish fish samples were rich in the omega-3 PUFA docosahexaenoic acid (DHA); 2. PUFA appear to be effective biomarkers indicative of different food sources in different locations. For example, gamma-linoleic acid (GLA) characteristic of blue-green algae, is significantly higher in Chinese fish muscle samples. 3. MeHg and MeHg/THg were significantly lower in Swedish zooplankton samples, but significantly higher MeHg and MeHg/THg in fish samples as compared to the samples from China; 4. There was a statistically significant negative correlation between MeHg and PUFA, monounsaturated fatty acids (MUFA), saturated fatty acids (SAFA), and terrestrial fatty acids in fish samples from oligotrophic lakes in Sweden. The same trend was not observed in samples from eutrophic lakes in China.

Overall, these data begin reveal the complexity of how food web structures influence regional and global differences in the bioaccumulation of Hg.

2h: Mercury cycling in response to ecosystem perturbations

RP-114

STABILIZATION OF RESIDUAL ELEMENTAL MERCURY FOLLOWING THERMAL REMEDIATION USING GASEOUS SULFUR

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In this study, the effectiveness of using gas-phase sulfur as a stabilization enhancement following in-situ thermal remediation of elemental mercury is evaluated. In-situ thermal remediation involves the application of heat and vacuum to remove volatile contaminants from the subsurface. Thermal remediation is a mature technology that is commercially available for targeted cleanup of subsurface volatile organic contaminants and is being evaluated as a viable treatment technology for elemental mercury by several research groups. Laboratory experiments have demonstrated that 99.8% of elemental mercury can be removed using in-situ heating at temperatures of 244-259°C. A field-scale deployment by one group of researchers demonstrated a fourfold increase in Hg removal relative to ambient conditions, by increasing the subsurface temperature to 50-55°C. Moreover, results from numerical simulations indicate that phase transitions that occur with increasing temperature can lead to complete vaporization of elemental mercury below the boiling point of water. Although thermal remediation appears viable for substantial Hg mass removal, small residuals are likely to remain in the subsurface following deployment. These Hg residuals will likely exceed environmental thresholds, thus requiring a combined remedial solution that includes large-scale mass removal with an in-situ stabilization component. In this study the immobilization of residual elemental mercury in the subsurface with a sequestering agent (vapor-phase elemental sulfur) is examined. The novel process utilizes residual heat that is present within the system following in-situ thermal remediation to deliver gaseous sulfur, resulting in the in situ formation of recalcitrant mercury sulfide species. Conceptually the process is simple with elemental mercury and elemental sulfur reacting in the gas phase to form the recalcitrant solid phase species. Simulations indicate that the role of oxygen is significant, especially if atmospheric air is used as the delivery mechanism. These simulations indicate that a reducing environment (i.e. a transport gas with depleted oxygen) is needed to form the targeted mercury sulfides. When considering the role of other elements present in the subsurface, our simulations identified the potential formation of iron sulfide (pyrite) that will acidify the soil as moisture and oxygen enter the system. The acidification potential can be overcome by judicious selection of the transport gas used to deliver elemental sulfur. Simulations indicate that with the proper selection of the transport gas, a buffered system can be established with redox conditions that favor the targeted stabilization reaction.

RP-116

SOIL-WATER METHYLMERCURY FLUX FROM NEWLY FLOODED WETLAND AND RIVER VALLEY SOILS

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Methylmercury (MeHg) production in newly flooded soils has been shown to be strongly related to soil organic carbon content. New hydroelectric developments and reservoir creation are being proposed in many ecosystems, but no data exists on whether MeHg flux from soil will vary with carbon content and composition. This information is essential to assess the environmental and human risks prior to reservoir creation. To address this knowledge gap for a hydroelectric power development under construction near Muskrat Falls on the Churchill River (Labrador, Canada), we collected 27 soil cores (15 cm long) from 3 sites for MeHg flux experiments. The core incubations included pre-flood soils, infrequently flooded soils, and wetland sites. Additional incubations with pre-flood soil cores included: 1) leaf litter layer removed, and 2) leaf litter layer and top 5 cm of soil removed. Each soil type and manipulation was replicated using three cores and flooded with Churchill River water, which was replaced every 24 hours. We sampled overlying water for MeHg analysis at intervals of 3 to 12 days for a period of 6 weeks. In previous flux core experiments using Muskrat Falls soil with leaf litter layer removed, we observed a 14-fold increase in MeHg concentration after only 5 days of incubation. We projected a 10-fold increase in riverine MeHg levels associated with flooding of the Muskrat Falls reservoir based on the relationship between soil organic carbon and soil MeHg for other systems. This resulted in a projected factor of 2.6 increase in MeHg in downstream Lake Melville estuarine surface waters, and an expected doubling of mean Inuit MeHg exposure. Our work suggests that soil organic carbon content is a useful screening criterion for hydroelectric power site selection, and that carbon removal could help reduce environmental MeHg concentrations associated with flooding. Plans for additional work at the Muskrat Falls reservoir site include soil characterization, water column MeHg measurements, MeHg flux core experiments with different levels of soil organic carbon, and probabilistic modeling to refine prior impact assessments.

RP-117

ANTHROPOGENIC AND NATURAL FACTORS AFFECTING THE INPUT OF LABILE MERCURY INTO MARINE COASTAL ZONE

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The important pathway of terrestrial Hg transport into marine ecosystems is the atmosphere, however in the coastal zone, rivers represent the main source of this metal. Hg emission in the Baltic region at the beginning of the 21st century was about 20% - 30% lower than during the 1980s. The climate warming, particularly in the autumn-winter season, is another factor contributing to the decline in Hg emission from the main source, the burning of fossil fuels, into the coastal zone of the southern Baltic. On the other hand, warmer winters result in a lack of icing or its persistence for a shorter period of time, thus giving more time for remobilization of Hg and its incorporation to the marine trophic chain. In addition extreme events, such as storms, heavy rains, floods, the erosion processes along the coast are more frequent. In consequence higher load of Hg is introduced to the sea. The toxicity of mercury depends on its form, therefore the aim of this study was an estimation of input of labile mercury to the coastal zone, under the influence of intensive precipitation, catchment management strategies and erosion of the coast. Samples were collected in years 2015-2017 in the Gulf of Gdańsk watershed (southern Baltic). Mercury fractions (labile and stabile) were analyzed with DMA-80 mercury analyzer using thermodesorption method. The obtained results show that during present days, when anthropogenic emission is significantly reduced, extreme events, such as intensive precipitations, floods, coastal erosion and development of catchment area are important factors for Hg bioaccumulation in marine trophic chain.

RP-118

IMPACT OF INTENSE RAINS AND FLOODING ON MERCURY RIVERINE INPUT TO THE COASTAL ZONE

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Mercury input from rivers to the coastal zone depends on local sources of this metal, and is regulated mostly by land use and meteorological events. This study focused on four small rivers, typical for southern Baltic, with no significant mercury sources, transporting mostly Hg originating from atmospheric deposition. Samples were collected from 5 stations in Zagrska Struga and Gizdepka, 4 in Płutnica and 7 in Reda river catchment. Station represent most common land use types forest, agriculture, wetlands and urban areas. Samples were collected during average flow conditions in four seasons for two years, additionally, water was sampled during selected meteorological events floodings, downpours, snowmelt and draught. Samples included filtered and unfiltered river water, which was analysed for total mercury using CV-AFS Tekran 2600. Additional analyses included DOC, temperature, pH, dissolved oxygen and conductivity. Additionally, flow was measured by current meter. To evaluate mercury retention in the catchment, rainwater mercury concentrations were measured, and for the estimation of relative importance of small river mercury input for the Baltic, water from one of the largest rivers, Vistula, was sampled near mouth.

Results show decreased mercury retention and greater input during intense rainfalls, and floodings, showing mercury elution from catchment. This suggests that relative importance of mercury input from smaller rivers may increase due to Climate Change, which in the boreal environment may lead to more frequent extreme events.

RP-119

IMPACT OF WARMING SURFACE FRESH WATERS ON MERCURY CYCLING AND ACCUMULATION IN FISH

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Rising air and water temperature have been reported worldwide. Predicted increases in water temperature for temperate waters by 2100 are between 1.5 and 4.5°C. Similarly, water temperatures in the majority of Canada are predicted to increase by 5–10°C by 2100. We

experimentally studied the impact of warming surface fresh waters on mercury cycling and accumulation in fish. Twelve tubs were filled to 8 cm depth with natural sediment collected from a lake in the Canadian Shield region, and filled with reverse osmosis filtered water to 40 cm depth. To simulate the effects of warming waters, four temperature settings with three replicates each were implemented: 12°C (baseline), 8°C (cooling), 16°C and 20°C (warming). These temperatures also cover the optimal range for white sucker, fish species used in the study. After 4 weeks, about 110 g of lumbriculus (food for fish) and sixty-five juvenile white suckers reared in the laboratory were added to each tub. The experiment was then run for 8 more weeks.Tubs were weekly topped up with reverse osmosis water to the initial volume to compensate for the evaporation loss. Water chemistry parameters, namely teperature, dissolved oxygen, pH and conductivity were measured daily, while hardness was measured weekly. Every week, three water samples from each tub were collected using a clean-hand dirty-hand procedure and acidified to 1% with ultrapure hydrochloric acid (HCL) for analyses of total and methylmercury concentrations. Five fish were randomly collected from each tub on a weekly basis and measured for length and mercury. Fish mortality was monitored daily and dead fish were removed. Observed changes in water chemistry, as well as total mercury and methylmercury concentrations in water, sediment and fish with time under the influence of varied water temperatures will be discussed.

RP-121

WATER QUALITY RESPONSE TO FLOW MANIPULATION IN A HG-CONTAMINATED CREEK

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East Fork Poplar Creek (EFPC) in east Tennessee, USA, was contaminated with large amounts of Hg between 1950 and 1963. Small amounts of Hg continue to be released from the primary source located at the headwaters of the creek. Stream restoration activities since 1983 included the initiation of a flow management program in 1996 to restore minimum baseflow in the uppermost reaches of the creek by pumping in uncontaminated water from a nearby lake. This water constituted ~13% of the baseflow measured at a point 21 km downstream but delivered substantial loads of dissolved organic carbon (DOC)(~25 kg/d) and total suspended solids (TSS)(166 kg/d).

We conducted water sampling along the length of EFPC on a monthly basis during 2011-2012 to assess patterns in Hg and monomethylmercury (MMHg) concentration along with ancillary water quality parameters (e.g., nutrients, DOC, TSS). Hg concentration decreased and MMHg concentration increased with distance downstream and MMHg concentrations were higher in spring and summer versus autumn and winter.

Upon cessation of the flow management program on 1 May 2014 monthly longitudinal sampling was repeated to determine what, if any, changes in Hg or MMHg might occur. Since cessation of flow management the Hg solid-water partitioning coefficient (Kd) has decreased by up to an order-of-magnitude throughout much of EFPC due to both lower solid phase concentrations and higher dissolved Hg (HgD) concentrations. pH values are slightly lower since flow management ended but remain in the range 7 8.3 where Hg sorption is relatively insensitive to pH changes. DOC concentrations have been more variable but are generally comparable to the earlier survey. Specific UV-absorbance at 254 nm (SUVA254), a measure of dissolved organic matter (DOM) composition, has increased.

Higher HgD concentration has potential implications for bioavailability and MMHg production. Total and dissolved MMHg concentrations have increased in EFPC and these increases are most pronounced during spring and early summer when biota may be more susceptible to exposure and uptake. Similar MMHg concentrations have not been seen in 20 years and in some locations are the highest on record. Other watershed-scale factors likely contribute to the observed patterns as these changes occurred over months rather than instantaneously after flow management stopped. Nevertheless, similar changes in MMHg have not been observed in a tributary to EFPC.

RP-122

IMPACT OF TIMBER HARVEST ON MERCURY WITHIN A LOBLOLLY PINE FOREST AND STREAM IN MISSISSIPPI

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Whereas forestry provides numerous benefits for humans and wildlife, forest harvest has been hypothesized to increase mercury (Hg) mobilization to aquatic systems. Mercury tends to accumulate in the upper layer of forest soil, where it associates with organic matter. This top soil can be disturbed by clear-cutting and the exposed soil is susceptible to runoff. Harvest may also change the net balance between methylation and demethylation through addition of carbon sources from decaying logging residues. To better understand the impact of timber harvest in a mixed pine and hardwood forest in the southeast United States, we measured Hg in soil, sediment, and water from the forest floor, a forest stream, and a nearby lake before and after harvest. We also determined methylmercury (MeHg) in the stream and the lake that it flowed into. Mean concentrations of THg in the top two cm of soil from sites transecting the forest floor decreased from 52.3 ± 4.3 ng/g before harvest to 36.0 ± 3.6 ng/g after harvest (±95% CI, n=14). The post-harvest reduction in Hg in the surface soils may be due to a combination of factors including mixing of surface soil with deeper soils that have lower Hg concentrations, an increase in runoff, and increased Hg volatilization stemming from higher soil temperatures and/or direct sunlight. Soil-Hg levels varied with particle size, with organic matter content having a greater influence than particle surface area. Sequential extraction of soil showed a significant decline in the percent of Hg bound to the oxidizable fraction, which includes organic matter known to complex Hg. In the lake, concentrations of THg and MeHg increased in the month following harvest. THg increased from 0.82 to 5.0 ng/L and MeHg increased from 0.04 to 0.17 ng/L. In the stream, dissolved THg decreased after harvest from ~3 to ~1.5 ng/L. Dissolved MeHg was similar before and after harvest (0.48 and 0.40 ng/L, respectively), but the proportion of MeHg increased in the stream from 10 to 30%. A methylation rate study is needed to fully address impacts of timber harvest on in-situ production of MeHg. In any case, an unharvested stream riparian zone likely served as a buffer retaining Hg and organic matter, and minimizing impacts to the stream and lake.

RP-123

EXPLORING THE EFFECTS OF TEMPERATURE AND RESOURCE LIMITATION ON MERCURY BIOACCUMULATION AND GROWTH IN FUNDULUS HETEROCLITUS USING DYNAMIC ENERGY BUDGET MODELING AND BEHAVIORAL ASSESSMENT

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Global climate change is likely to affect both temperature and resource availability in aquatic ecosystems. While higher temperatures may result in increased food consumption and increased mercury accumulation, they may also lead to increased growth and reduced mercury tissue concentration through somatic dilution. Dynamic energy budget theory provides a broad and generalizable framework based on first principles of energy metabolism that is well suited to understand these interactions, allowing joint acquisition and interpretation of chemical exposure and stressor effect information to be translated into demographic rate changes. In the current study, we conducted growth and bioaccumulation experiments to examine the interaction of temperature and resource availability on mercury accumulation and effects in the estuarine fish Fundulus heteroclitus (mummichog). In the first experiment, juvenile mummichog were fed 3.3% or 10% of their dry body weight/day with tuna naturally contaminated with mercury and held at either 15 or 27°C for 28 days. Growth was low in most treatments, except in fish fed 10% body weight held at 27°C (40% weight and 12% length increase). However, methylmercury bioaccumulation was similar across feeding conditions but increased with temperature (~17-fold increase in methylmercury concentration at 27°C and ~7-fold increase at 15°C, regardless of feeding rate). In the second experiment, mummichogs from two wild populations with differing native mercury exposures were fed either a high or low methylmercury diet. Fish were strip-spawned every two weeks during the feeding period. Adults were sampled for total mercury concentration at the start and end of the experiment, and egg methylmercury concentration was measured in unfertilized eggs from each spawning event. Danioscope software was used to assess the heart rate of developing embryos at 10 days post fertilization. A dark:light movement assay determined differences in behavior of larvae between treatments at three and 10 days post hatch using Ethovision software. Tissue analysis indicated successful maternal transfer of mercury to eggs in the high mercury feed treatment. Heart rate and movement assays indicated potential population level differences in baseline behavior. The use of these data in a dynamic energy budget model may greatly aid in understanding how temperature and resource availability affect mercury bioaccumulation. Overall, this work contributes to the ongoing development of an ecological modeling framework in a fish with an extensive toxicological and genomic background. Ultimately, we are working to connect molecular mechanistic, physiological, reproductive, and behavioral responses to population level fitness.

RP-124

MICROBIAL ACTIVITY AND DIVERSITY, SOIL ENZYMES, MERCURY AND ARSENIC SPECIATION INDICATORS OF QUALITY RESTORATION IN FRENCH GUIANA OLD MINING SITES

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Gold mining activities in Amazonian rainforest lead to deforestation since decades and also to pollution with the use of mercury, arsenic and cyanide during the extraction process. While ecological rehabilitation is essential to restore biodiversity and decrease erosion on deforested lands such as mining sites, few studies point out the behavior of toxic traces elements such as mercury or arsenic during the rehabilitation process as well as their toxicity. Our original study focused on the potential use of microbial parameters related to C, N and P turnover, functional diversity, soil chemical proprerties and sequential extraction of Hg and As, to assess ecological impact and quality of revegetation processes of old mining sites affected by long-term acid and metal stress. We sampled two plots revegetated since 18 years in the site of Yaoni, in French Guyana. The first (R) revegetated with leguminous species (Clitoria racermosa and Acacia mangium), the second revegetated with spontaneous vegetation (Sv). We performed a microcosm experiment of soil in controlled conditions during 30 days where soil characteristics and mercury and arsenic speciation were analyzed. Along the incubation, microbial biomass, carbon, nitrogen and phosphorous mineralization processes and enzyme activities (FDA, dehydrogenase, β-glucosidase, urease, alkaline and acid phosphatase) were estimated to characterize the soil functional diversity and metal stress.

Our results showed that revegetation with leguminous (R) had a positive and significant effect on soil chemical quality, soil microbial biomass, mineralization rates of C, P, and on enzyme activities involved in C and P cycles. Revegetation process had however no effect on N mineralization and urease activity which suggested a metal stress in these conditions. Revegetation process had a significant effect on Hg speciation. In R the major proportion of Hg is bound to organic matter phase and few bound to iron oxide one. While in Sv we found more mercury mostly associated to iron oxide phase, and significantly to exchangeable and soluble Hg representing the more available carrier phases. Difference in revegetation process had less effect on As speciation. Statisticals analysis demonstrated that exchangeable Hg, total As and soil pH are key stress factors for biological parameters in rehabilitated lands.

These results also suggested that microbial activity, enzymes activities and mercury cycle are sensitive to land rehabilitation, which confirm our hypothesis that mercury speciation, microbial activity and enzymes activities must be evaluated as parameters for revegetation process quality.

RP-125

METHYLMERCURY PRODUCTION RESPONSE TO WETLAND CREATION AT KELLY'S SLOUGH NATIONAL WILDLIFE REFUGE, NORTH DAKOTA

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Established in 1936, Kellys Slough National Wildlife Refuge (KSNWR) is a 5.1 km2 managed grassland and wetland complex located near Grand Forks, ND. In the early 1990s water control structures were constructed on an intermittent stream located within the refuge to create standing water conditions that support migratory waterfowl and shorebirds. This along with excavation of some surface soil resulted in a complex of three interconnected open-water pools: upper pool 1 [UP1], lower pool 1 [LP1], and lower pool 2 [LP2]. Immediately above the inlet to UP1, stream inflow passes through Pender pool (PP), a dense cattail marsh that was unintentionally formed during either pool or road construction at the site. A concern for the refuge managers is the observation from mercury (Hg) researchers that creating impoundments can lead to elevated levels of toxic methylmercury (MeHg), and that manipulating water levels so that sediments are alternatively dried and rewetted can further stimulate MeHg production, via sulfate re-oxidation. Starting in June 2014, the US Fish and Wildlife Service and US Geological Survey initiated a study of KSNWR to address these concerns. Surface water samples were collected from the three distinct pools during ice free periods in 2014 2016, and a sampling site was added at the inlet to Pender pool in 2015. Water samples were analyzed for total Hg, MeHg, and dissolved organic carbon (DOC) at the US Geological Survey Mercury Research Lab in Middleton, Wisconsin. Filter passing MeHg (FMHG) concentrations increase an average 1.5X (range 0.5 5.5X) and percent of total mercury that is methylmercury increases an average of 1.3X (range 0.5 3.7X) from the inlet to the outlet of PP., suggesting that Pender pool is a source of FMHG to the downstream complex. Spatial trends of DOC show decreasing concentrations from the inlet to outlet of the study area, indicating that inflowing surface water is an important source of DOC to the system. Within the complex, average concentration of FMHG is highest at the inlet to UP1 and decreases in a downstream direction, which is likely due to photo-demethylation and reduced primary production in response to lower nutrient conditions. In addition, observed increases FMHG concentration between LP1 and LP2 during spring and early summer suggests that this part of the complex serves as a location of net MeHg production. Given that this location experiences the greatest range of water level manipulation, we surmise the MeHg increases are in response to seasonal wetting and drying of bottom sediment.

RP-126

INCREASES IN FISH MERCURY FROM HISTORICALLY IMPOUNDED AND NEARBY REFERENCE WATER BODIES OF NORTHERN MANITOBA

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We have analyzed a database of fish muscle Hg concentrations from water bodies in northern Manitoba, Canada, in order to determine the extent of long-term recovery toward pre-impoundment levels in the decades that have elapsed since reservoir flooding for hydroelectricity generation. To date we have examined available data from 1971 2012 for walleye (Esox lucius), northern pike (Sander vitreus), and lake whitefish (Coregonus clupeaformis) species collected from 22 northern boreal water bodies.

The water bodies examined in this study include several flooded during the diversion of the Churchill River flow in the 1970s to augment the flow of the Burntwood-Nelson River System for electricity production. Prior studies have identified the extent of area flooded during impoundment as the major determinant of an initial increases in fish muscle Hg for these three species, ranging from 100 to 700% of background levels, within 2 -14 years of initial impoundment. The mechanism of the Hg increases is thought to be enhanced decomposition of organic matter in newly flooded regions, which promotes Hg methylation and entry into aquatic food webs.

Despite large variations between reservoirs, we observed increases in walleye and northern pike Hg concentrations over the past decade in the majority of examined reservoirs. In most cases, these increases occurred in the past decade after minimum fish Hg levels were observed between 1998-2005.

In contrast to the historical increases observed soon after impoundment, the recent increases are not correlated to initial flooded area nor to estimates of organic carbon content of regional soils. Furthermore, the magnitude of observed increases in walleye and northern pike muscle Hg observed in non-regulated water bodies over the last decade can equal those in regulated water bodies. Preliminary analysis suggests that regional variations, including those enhanced by climate-driven changes in the hydrologic cycle, may elevate fish Hg concentrations and in turn exacerbate fish Hg burdens in regions impacted by regulation.

RP-127

OCCURRENCE OF MERCURY METHYLATION HOTSPOTS AFTER FOREST HARVEST

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Forestry activities have in several studies been identified to increase concentrations and loads of methylmercury (MeHg) in surface waters. There is, however, a great deal of variation in the magnitude of documented effects, varying from no effect up to manifold increases in MeHg concentrations and export. In contrast, studies of soils after forest harvest are very few. By combining molecular methods with soil geochemical analyses, we here examine how various forestry activities affect Hg methylating microbial communities and MeHg formation in soils. We investigated areas undergoing conventional stem-only-harvest and areas where both stem and stumps are removed to increase the share of bioenergy. We tested the hypothesis that environments of high MeHg net formation, so called Hg methylation hotspots, are more prone to form after stump-harvest than after stem-only-harvest. The reason would be more severe soil compaction and soil disturbance when stumps are removed. Soil concentrations of MeHg, percent MeHg of total Hg (THg) and bacterial community composition were determined at 200 sampling sites distributed across eight catchments in the north and south of Sweden. Each catchment was either stem-only-harvested (n=3), stem- and stump-harvested (n=2) or left undisturbed (n=3). A higher percentage of MeHg relative to THg was observed in one of the stump-harvested catchments. This catchment also featured the highest bacterial diversity and highest relative abundance of bacterial taxa known to include Hg methylators, such as sulfate- and iron-reducers. Environments showing high MeHg net formation and high share of microorganisms known to methylate Hg, i.e. so called Hg methylation hotspots, were most often associated with water-filled cavities created by stump removal or driving damage. We suggest limited oxygen supply in these environments in combination with access to labile carbon sources from logging residual may favor the activity of Hg methylating microorganisms and thereby enhance MeHg formation. Despite this observation, stump harvest did not cause increased concentrations of MeHg in the stream, indicating that soils with high MeHg concentrations were not directly connected to the stream. We suggest the large variability regarding forestrys influence on MeHg in runoff water reported in the literature is due to a combination of how forestry operations affect the net formation of MeHg and the hydrological connectivity between environments where MeHg is formed and surface waters.

RP-128

SYSTEMATIC REVIEW AND ASSESSMENT OF LINKS BETWEEN SULFUR DEPOSITION, SULFUR CYCLING, AND MERCURY CYCLING IN NORTH AMERICAN ECOSYSTEMS

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The latest review of the current secondary National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen and sulfur started in 2013. The scope of the review includes, but is not limited to, the atmospheric chemistry and ecological effects of sulfur (S) deposition. The Integrated Science Assessment (ISA) of relevant research is currently under development by the U.S. EPA and will provide the scientific foundation for review of the secondary NAAQS for oxides of sulfur and other closely related criteria pollutants. One of the subjects in the ISA is the link between atmospheric S deposition and mercury methylation within aquatic and wetland ecosystems. Relevant scientific literature was identified using machine learning and citation mapping based on the references included in the previous ISA addressing ecological effects of oxides of sulfur (published in 2008). Relevant literature was also identified by participants in an ISA Peer Input Workshop held in summer 2015. These approaches identified approximately 6500 papers published between 2008 and 2015 related to the non-acidifying effects of S deposition, and keyword searches and title screening within this set of publications identified 203 publications for detailed review. Recent research has expanded the geographic scope of inference of links between S cycling and methylmercury from the Northeastern peat bogs and lakes described in the 2008 ISA to now include streams, rivers, and freshwater marshes across the continental United States. Advances in microbial ecology have enhanced mechanistic explanations of mercury methylation. Observational studies, experimental S additions, and long-term field collections provide limited but coherent evidence of quantitative relationships between S and methylmercury production or concentration. Additional research or modeling could potentially identify dose-response relationships between S deposition and surface water sulfate concentrations, or between S deposition and methylmercury in the environment and in biota. The views expressed in this abstract are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

RP-129

THE LEACHING OF MERCURY FROM SOILS AND ITS INFLOW TO THE SEA DUE TO INTENSE PRECIPITATION

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For several years mercury has been recognized as a one of the most dangerous world pollutants. Despite all the restrictions related to the limitation of introducing of Hg into the environment, the concentration of the metal is still at a high level. The Baltic Sea is a relatively small water body and it should be taken into account that rivers are the main source of mercury there. Due to this, the size and management of river basins have a huge impact on the level of mercury contamination in the coastal region. Soil can be considered the main sink of natural and anthropogenic mercury. Moreover, in relation to changing climate, the growth of concentration of Hg was recorded. It was caused by intense rainfall enhancing surface runoff and leaching of mercury from soil to the river water. The aim of that work was to estimate the impact of seasonal changes and intense precipitation on the leaching of labile form of Hg from soils.

The samples were collected in the Reda river (the longest river of the Pucka Bay basin (southern Baltic Sea)). These rivers where divided into 7 stations characterized by different levels of development of the basin. The material was collected seasonally in 2015 year from three depths of soil layer (0-20cm, 20-40cm, 40-60cm) and from river sediment. The fractionation of mercury was carried out by thermal desorption by DMA analyzed. Due to the combustion of the samples in different temperatures, the labile and stable form of mercury were detected.

The Reda river was characterized by high content of labile form of mercury in all studied stations. Take into account individual stations, a twofold increase of labile form of Hg in source of Reda river after flooding was detected. The leaching of labile mercury from soil and transfer to the river sediment was caused by the growth of the water level in the river. The significant increase of this form was noticed in the other stations as well. It was connected with content of fine grain and organic matter. The intense precipitation changed in the contribution share in both stable and labile form of mercury in soil and sediment of the Reda river.

RP-130

A MECHANISTIC MODEL FOR MERCURY CYCLING AND BIOACCUMULATION IN NEW RESERVOIRS

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Flooding has been well documented to result in increased fish mercury concentrations. Peak concentrations in adult sportfish such as northern pike or walleye can be up to 7 times greater than background levels in some new reservoirs. A mechanistic model of mercury cycling and bioaccumulation in reservoirs (RESMERC) was developed and initially calibrated using data from a series of whole-ecosystem mercury/greenhouse gas experiments at the Experimental Lakes Area (ELA) in Ontario, Canada. The ELARP experiment flooded a boreal wetland, while the FLUDEX experiment flooded three boreal forest upland sites with contrasting moisture conditions, vegetation, and stores of organic carbon. The model was then applied to two full scale reservoirs: Notigi Reservoir in Manitoba and Robert Bourassa Reservoir in Qubec. Model calibration included components for hydrology, carbon decomposition in flooded soils and sediments, and inorganic Hg(II)/methylmercury fluxes and concentrations. The model calibration reproduced several key trends observed at the ELA sites, including the rapid increase and subsequent decline of MeHg levels observed for the upland sites (FLUDEX) and sustained MeHg production in the wetland environment (ELARP). Observations and simulations suggested a pulse in decomposition after flooding that led to a pulse in MeHg production lasting a few years in flooded uplands, and longer in the flooded wetland. Large increases in porewater Hg(II) were observed for the medium carbon FLUDEX site shortly after filling. Simulations suggest that this was driven by DOC increases and that Hg bound to DOC in porewater is methylated. When the model was applied to Notigi Reservoir, the calibration based on the ELA sites resulted in peak mercury concentrationsfor northern pike and walleye that were too low, and a predicted recovery that was too fast (e.g. 10-15 years), compared to the observed 20-30 year recovery period. The model was recalibrated to fit observed fish mercury levels in Notigi and Robert Bourassa Reservoir well, but this calibration did not represent FLUDEX results adequately. There may be additional processes in full scale reservoirs with hypolimnetic waters that are not reflected in FLUDEX and ELARP, which represented shallower floodzones with seasonal water level fluctuations. Sensitivity analysis predicted that in addition to the extent of flooding and type of terrain flooded, flowrate is an important consideration when predicting the response of fish Hg levels following reservoir creation. Rapid water throughput has the potential to reduce peak MeHg levels.

RP-131

WHY DO FISH MERCURY CONCENTRATIONS INCREASE IN HELLS CANYON COMPLEX? A CONCEPTUAL MODEL

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The Hells Canyon Complex (HCC) consists of three hydroelectric facilities and associated reservoirs along a 145 km stretch of the Snake River on the Idaho-Oregon border (USA). Brownlee, Oxbow, and Hells Canyon Reservoirs went into service between 1958 and 1967, have surface areas of 4.6 to 59.1 square km and maximum depths from 25 to 91 m. Other human influences affecting the study area include increased regional and global atmospheric mercury (Hg) emissions since the 1800s, Hg mining in the upstream watershed that began in the mid-1800s, upstream agriculture since the 1900s, and the operation of a large cement kiln roughly 15 km from HCC, since 1979. These activities have increased Hg loading to the river system and altered conditions related to hydrology, particle dynamics, nutrient loads, system productivity, and water quality. Fish sampling in 2013-2015 clearly showed that Smallmouth Bass Hg concentrations in HCC increased progressively through the three reservoirs and declined in the Snake River downstream of the complex. Mercury concentrations in Smallmouth Bass (>250 mm) in Hells Canyon Reservoir were 0.266 µg/g, 4.4X greater than concentrations of ~0.061 µg/g in the Snake River immediately upstream of HCC. Brownlee and Hells Canyon Reservoirs are listed as impaired for Hg by the States of Idaho and Oregon. Deep water pumping from HCC has also been considered to improve downstream cold-water fish habitat, but there are concerns regarding the fate of high levels of methylmercury (MeHg) observed in hypolimnetic waters of HCC (up to 2.9 ng/L in Brownlee Reservoir and 5.5 ng/L in Hells Canyon Reservoir), if a pumping strategy were to be implemented. The U.S. Geological Survey and Idaho Power Company are collaborating on a study to better document total Hg and MeHg levels in HCC and downstream, understand factors controlling their spatial and temporal distribution, and ultimately explore remedial options. A conceptual model of Hg cycling and bioaccumulation in HCC will be presented. A leading hypothesis to explain elevated MeHg in HCC food webs is that elevated inputs of nutrients and organics enhance the supply of labile carbon, which serves as a substrate for Hg(II)-methylating microbes in deep zones of the system. Other possible contributing factors include Hg inputs from legacy Hg mining in the watershed and legacy/ongoing Hg inputs from the other nearby air and watershed sources.

RP-132

MERCURY EMISSION FROM WASTEWATER IRRIGATED SOIL IN CHINA

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With the industrialization and urbanization after the adoption of reform and opening-up policy in China, industrial and domestic wastewater has been widely produced and released into rivers, and has been used to irrigate cultivated soil due to its rich nutrient substances. Therefore, mercury (Hg) in the wastewater irrigated soil could become an important emission source of Hg to the air. In this study, we investigated and sampled surface soils from 13 traditional wastewater irrigated fields which had more than 20 years irrigation history. A continuous flow chamber was designed to simulate the emission of Hg under different temperature and solar irradiation in lab. By measuring the total gaseous mercury (TGM) concentration in the chamber, the emission rate has been calculated. We estimated that TGM emission to the air from 38 major wastewater irrigated fields in China is 2019±404 kg per year. The emission rate has a strong positive correlation with temperature and solar irradiation, respectively. Also, contents and speciation of Hg in the irrigated soils were determined and discussed. Due to wastewater irrigation, the THg concentrations in the irrigate soil range from 166±12 ng/g to 10089±72 ng/g. Most of them are much higher than the background values of Chinese soil. Our study shows that Hg emission from wastewater irrigated soil in China should not be ignored.

RP-136

CONCENTRATION, REACTIVITY AND BIOAVAILABILITY OF MERCURY IN WILDFIRE ASH

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Wildfire has been increasing in frequency, size and intensity in recent decades due to climate change and increasing fuel loads, and these trends are expected to further rise in the future. There are many studies showing that mercury (Hg) is lost from forest ecosystems to the atmosphere due to wildfire. However, few studies have examined residual pools of Hg after wildfire, namely surface ash, which can contribute dissolved and particle-bound Hg to aquatic ecosystems upon runoff and erosion. Specifically, the Hg contents in different ash types, and more importantly the reactivity and bioavailability of Hg in ash, are largely unknown. In the present study, we quantified Hg contents and investigated the reactivity and bioavailability of Hg in different ash types generated from two wildfires in northern California (Wragg Fire and Rocky Fire in summer 2015). Black ash (200−500°C) and white ash (>500°C) were collected from multiple locations within the burn perimeter before any rainfall/leaching events. Two acid digestions were used to extract Hg from each ash sample: nitric acid/peroxide (reactive Hg) and aqua regia (reactive and non-reactive Hg). The difference in Hg concentrations between these two digestions was operationally defined as the non-reactive Hg pool. All ash samples contained measurable but highly variable Hg contents, ranging from 4 to 125 ng/g (n=28). Overall, the black ash had a median Hg concentration (based on aqua regia digestion) of 29 ng/g (n=14) compared to 14 ng/g in white ash (n=14). Regarding the reactivity of Hg, we found that compared to litter samples (unburned sites), the majority of black ash and white ash samples contained much larger pools of non-reactive Hg, indicating that wildfire altered Hg reactivity in the ash. Further, we performed a sealed-bottle incubation experiment in which litter, black ash, or white ash was incubated with fresh surface water for 4 and 12 weeks. Preliminary data indicated that Hg in litter was highly soluble and efficiently methylated by anaerobic microbes inside the incubation bottle. In contrast, we observed very small amounts of soluble Hg when black ash or white ash was incubated, and we detected almost no methylated Hg suggesting that Hg in ash is less reactive and bioavailable. Therefore, our work implies that Hg in ash may be less available for further biogeochemical transformation (e.g., methylation), which has important implications for the effects of wildfires on the risk of Hg to aquatic food webs and consumers of fish.

RP-137

WATERSCAPE EFFECTS ON NET MERCURY METHYLATION IN A TROPICAL WETLAND LANSCAPE OF THE AMAZONIA

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The periphyton associated with freshwater macrophyte rhizomes is the main site of Hg methylation in different wetlands in the world. The objective of this study was to test the use of water bodies connectivity metrics, in the context of landscape ecology, in a tropical wetland landscape (Guapor River, Amazonia, Brazil) as an indicator of net mercury methylation potential in periphytic communities. Fifteen lakes with different lateral connectivity patterns were sampled as well as the main channel of the river. We tested net mercury methylation potentials through incubations with local water and Eichhornia crassipes periphyton/rhizomes complexes, using 203HgCl2 as a tracer. Physical-chemical variables, landscape data (morphological characteristics, land use, types of lateral connection of water bodies) and field data were analyzed with Variation Partioning, and Generalized Additive Models (GAM). The Me203Hg net production (as% of 203Hg added) was expressive (6 - 26%). The model that best explained variations in the net production of Me203Hg (76%) was constructed by the variables: lateral connection type, total phosphorus and dissolved organic carbon (COD) in water. The type of connection was the best factor to the model fit (r2 = 0.32, p = 0.008) and the temporarily connected lakes showed higher rates of net mercury methylation. Both COD and total phosphorus showed significant covariance with mercury methylation rates (r2 = 0.26, p = 0.008 and r2 = 0.21, p = 0.012 respectively). Our study proposes a strong relationship between net MeHg production rates in tropical areas, the type of water body and its hydrological connectivity within the aquatic landscape.

RP-138

CHARACTERIZATION OF THE MACROPEDOFAUNA AND ITS INFLUENCE ON THE CONCENTRATIONS OF HG IN SOIL UNDER AGROFORESTRY SYSTEM IN THE SOUTH OF AMAZON

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The agroforestry system (SAF) is a land use category, that integrates in the same geographic space: perennial woody plants with crops and / or animal breeding. This farming system has been identified as strategic in the mitigation of greenhouse gas emissions (GHG) is an alternative use of the land capable of reducing mercury remobilization adsorbed on leaf tissue of native or cultivated vegetation. In this context, the objective of the present study was to assess the influence of macro invertebrate soil on mercury concentrations in deployed agroforestry system under red ultisol in the Umari rural settlement, South of Amazonas state. Four methods were used: i) digital image processing and production of thematic maps; ii) demarcation of fixed plots and construction of soil monoliths; iii) determination of Hg concentrations in soil and individuals of the macro invertebrate soil; and iv) statistical analysis. A total of, 11 groups of macro soil invertebrates, especially in the layer of 0 -10cm depth of soil. The dominant groups of soil invertebrates were: Oligochaetas (72.32%), Diplpodes (miripodes) adults and young (13.20%), Isoptera anaplotermes (5.66%) e Arachnida (2.51%). Among these, in descending order, high [Hg] were recorded in Oligochaetas (19.337 ng/g), Larvas de Diplpodes (16.939 ng /g), Arachnida (781 ng / g) e Chilopoda (445 ng / g). The average concentrations of mercury in the soil compartment (0-10cm depth) varied of 38 ng / g and 292 ng / g In the rainy season and 22 ng / g an 219 ng /g In the dry season. Among land use systems assessed (shifting cultivation, livestock and agroforestry system), the agroforestry systems with (SQF) ten years or more of deployment presented greater diversity of macrofauna taxonomic groups of the soil and, the same time high levels of Hg (Med. 286.5 ng / g) in soil and macrofauna of soil. On the other hand, the conventional farming systems with low diversity of soil invertebrate groups, had lower [Hg] in the soil and in soil macrofauna individuals. These results demonstrate the potential of the agroforestry system to retain Hg and potentially other heavy metals, from natural and / or anthropogenic sources. furthermore, the presence of macrofauna of the soil tends to favor the fixation of Hg among other substances the natural ecosystem and cultivated southern Amazon.

RP-139

METHYLMERCURY IN AN INTERMEDIATE FEN PEATLAND – SPATIAL AND TEMPORAL PATTERNS AND IMPLICATIONS FOR CLIMATE CHANGE

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Northern peatlands can be sites of net methylmercury (MeHg) production and sources of MeHg to downstream aquatic ecosystems. Northern peatlands are 'hot spots' of MeHg production and transport because of their anoxic organic peat soils that support sulphate-reduction and hence, mercury methylation. Northern peatlands are not a single ecosystem type, but are a continuum of hydrological connectivity and nutrient status (nutrient-rich, groundwater-fed fens to nutrient-poor, rain-fed bogs). Although they are all peat accumulating systems, fens tend to be dominated by vascular plants (e.g. sedge spp.) while bogs are moss-dominated (typically sphagnum spp.). Although a considerable number of intensive studies on MeHg have been undertaken on nutrient-limited, moss dominated peatlands, no intensive field studies have been undertaken to evaluate patterns and controls on MeHg concentrations in circumneutral pH, sedge-dominated fen peatlands. We investigated pore water and stream total mercury (THg) and MeHg along with other hydrochemical parameters in a boreal intermediate fen in northern Ontario, Canada to evaluate the overall distribution of MeHg and to assess whether or not within-peatland near-stream zones of potential groundwater-surface water interaction had higher MeHg concentrations than more hydrologically decoupled areas of the peatland. Pore water sampling was conducted monthly during the summer and fall 2016 at both higher resolution transects (8 m length) near incised fen streams and lower resolution transects (190 ± 65 m length) across the broader fen area. A clear pattern of greater net MeHg production near incised fen streams than the broader area of the peatland emerges as a result local groundwater discharge as indicated by other water chemistry and hydraulic head measurements. The proximity and high degree of hydrologic connectivity of near-stream pore waters to the streams represents an important linkage between net MeHg production and transport to downstream aquatic ecosystems in these understudied peatland types. It has been suggested that climate change has the potential to shift northern peatlands toward more vascular-plant dominated ecosystems, so greater insight into their Hg biogeochemistry will contribute to the broader understanding of Hg in northern aquatic ecosystems in the future.

RP-140

INFLUENCE OF CAGE AQUACULTURE ACTIVITY ON THE DISTRIBUTION AND METHYLATION OF HG IN A RIVER-RESERVOIR SYSTEM, SOUTHWEST CHINA

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To understand the influence of cage aquaculture activity on the distribution and methylation in river-reservoir system, Wujiangdu (WJD) and Yinzidu (YZD) reservoirs which located in Wujiang River Basin, Southwest China, were chosen in this study. The WJD and the YZD are characterized by absent and popular cage aquaculture activities, respectively. Concentration and distribution of Hg species in different sectors of the river-reservoir system (e.g. water column, sediment, inflow-outflow rivers of reservoirs) were systematically investigated over a one-year period. On the basis of the measured data, a detailed Hg mass balance in selected reservoirs were developed as well.

Our results showed that the concentrations of THg in the WJD and the YZD present the same level. However, concentrations of MeHg in water column and sediment of WJD were significantly elevated compared to those of YZD, suggesting the active Hg methylation in the WJD. In contrast, no discernable Hg methylation was observed in the YZD during the sampling periods. The results suggest that high primary productivity resulting from cage aquaculture activities in the WJD is an important control on Hg methylation in the reservoir, increasing the concentrations of MeHg in water in the Wujiang River basin, southwestern China. Our Hg mass balance calculations showed that YZD represented a net sink of MeHg, WJD acted as a source for MeHg annually.

The YZD as a newly formed reservoir were not active sites of net Hg methylation because of the low organic matter in submerged soil. On the opposite, organic matter in surface sediment originating from cage aquaculture activities in WJD principally lead to a much more active net Hg methylation. Current study confirmed that MeHg production in reservoirs located in southwestern China cannot be predicted using previous observations in North America and Europe because the Hg methylation process in the Wujiang River Basin is driven by a completely different biogeochemical dynamic.

RP-142

A MOLECULAR APPROACH TO UNDERSTAND BIOAVAILABILITY OF METHYLMERCURY ASSOCIATED WITH VARIABLE SOURCES OF NATURAL DISSOLVED ORGANIC MATTER

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Coastal marine ecosystems have ecologic, economic, and social value, but they are threatened by human induced climate change and increased mercury (Hg) loadings. These changes may influence the bioaccumulation of methylmercury (MeHg) into aquatic food webs where it becomes an exposure risk to humans. The most important step for MeHg incorporation into the coastal food web is via phytoplankton uptake and assimilation. Uptake depends on the chemical form (speciation) of MeHg, and has been correlated to the concentration and composition of organic matter (OM) in the system. Specifically, terrestrially derived OM in coastal waters decreases MeHg bioavailability compared to that of autochthonous origin (here forward referred to as marine). Thiol ligands associated with dissolved OM (DOM) and particulate OM (POM) primarily control the chemical speciation and bioavailability of MeHg in oxidizing coastal waters, so we have hypothesized that differences between thiol composition or concentration may be controlling uptake via thermodynamic and kinetic constraints. To test this, DOM was extracted from water samples collected at discrete points along the NE coast of the United States that represent variable organic matter and Hg loadings. The overall binding strength of the DOM to MeHg was then quantified through competing ligand experiments using a low molecular mass thiol ligand as the competing ligand. DOM binding capacity was evaluated through S K-edge XANES measurements and speciation modeling. Our results provide a refined molecular level understanding of how MeHg speciation is influenced by DOM from various sources, and give insight towards the observed higher bioavailability of MeHg bound to marine compared to terrestrial DOM. Understanding these processes is critical for reliably predicting MeHg levels in marine biota, and human exposure, now and following expected human and climate driven ecosystem changes.

RP-143

OUTFLOW OF MERCURY FROM SOIL TO THE RIVER CAUSED BY RIVER ENGINEERING

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Many research indicate that in the catchments atmospheric Hg retention takes place. Deposited Hg is accumulated in the organic-rich soil where it effectively binds to reduced sulphur sites as well as with oxygen/nitrogen-groups in the organic molecules. However there are some factors which stimulate the outflow of Hg from soil to the river. The aim of this research was to assess the impact of the river engineering on the outflow of mercury from soil to the river. For this purpose in years 2015-2016 mercury concentrations were measured in precipitation, soil and also in water, sediment and SPM from rivers in different parts of the Southern Baltic coastal zone. Total Hg in liquid samples were analyzed by means of Tekran 2600 analyzer. The direct mercury analyzer DMA-80 was used for the detection of Hg in solid samples. Apart from total Hg concentration in solid samples, also four fraction of Hg were separated. Hg fraction associated with labile compounds such as: mercury halides, mercury perchlorate, mercury nitrate, mercury cyanide, mercury thiocyanate,mercury fulminate,mercury acetate,methyl mercury and humus-like substance (labile-1); mercury sulfate, mercury oxide (red) andmercury fluoride (labile-2) as well as with mercury sulphide (stabile-1) and mineral matrix (stabile-2) was analyzed using the thermo-desorption method.

The obtained results show that activities related to river engineering such as dredging, desludging and rebuilding of the riverbed had a significant effect on mercury outflow to the river. As a result of these actions significant increase of mercury concentration in water and sediment river was observed. Also the percentage contribution of mercury fraction in soil and sediment was changed. Elevated levels of mercury in the sediment remained during few next weeks. This indicate that catchment management affects the load and the form of Hg reaching the sea with surface runoff. While less important on a global scale, it is crucial in mediterranean seas and coastal zones, where rivers can be the main source of mercury.

RP-144

CONSTRAINING UNCERTAINTIES AND PROCESSES IN THE GLOBAL MULTIMEDIA MASS BALANCE OF MERCURY: UNDERSTANDING OCEANS IS MORE IMPORTANT THAN FURTHER UNDERSTANDING ATMOSPHERIC EMISSIONS

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Uncertainties in emissions and key kinetic processes such as reduction-oxidation (redox) reactions, mass transfer coefficients and partition coefficients limit our quantitative understanding of the global mercury mass balance. Such an understanding helps us comprehend how confident can we be in the results from global models. Also, research can then be directed towards most uncertain parameters or processes. At present, a substantial effort is made towards constraining anthropogenic emissions of mercury, particularly to atmosphere. Uncertainty around global atmospheric mercury emissions is generally accepted to be +/- 50%. However, it is also known that the uncertainty surrounding rate constants for reduction and oxidation span orders of magnitude, factor 10 to 100! This brings out the question if more research, and money, should be directed towards updating emissions or towards, for example, better understanding rate constants for reactions.

Recent GEOS-Chem publications attempt to constrain mercury emissions to the atmosphere using sensitivity analysis type updating of model results by using field observations of mercury. While this is important, a true uncertainty analysis should involve probabilistic Monte

Carlo sampling, and a Bayesian updating of key input parameters using all available mercury observations. Previously, Qureshi et al. (2011, Global Biogeochem. Cycles, doi: 10.1029/2011GB004068) had conducted a complete but unbounded Monte Carlo uncertainty analysis on the global mercury multimedia mass balance, including fluxes, transfer processes and compartmental inventories. Here, we use all the available observations of mercury and mercury species in air and water to bound the uncertainties in the global mass balance of mercury, and determine important influential parameters. A Markov Chain Monte Carlo technique called Metropolis Hastings is adopted. A priori uncertainties in model inputs, such as emissions, rate constants, partition coefficients, are determined from literature. Then 10,000 model runs are made, and uncertainties in inputs are refined based on the bounds forced by actual observations. Finally, a posterior distribution of inputs is obtained. This is used to calculate the refined and more constrained global mass balance of mercury and to determine influential parameters.

It is found that the uncertainties in key fluxes, such as evasion of mercury from ocean to atmosphere are reduced from factor 650 to factor 50, and in net reduction of Hg(II) to Hg(0) in atmosphere from factor 36 to 10. An important finding is that uncertainties in oceanic parameters such as redox rate constants, and the partition coefficients of mercury in surface oceans are much more influential than anthropogenic mercury emissions. Therefore, more efforts should be made on understanding oceans rather than emissions. This finding also questions the inferences from some global models that Asian emissions shoud be higher just because results do not match observations it could be because of rate constants!

RP-145

THE INFLUENCE OF NUTRIENT LOADING ON METHYLMERCURY AVAILABILITY IN ESTUARIES, LONG ISLAND, NY

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Although mercury dynamics have been relatively well-studied in freshwater ecosystems, they are understudied in estuarine environments. It is suggested that nutrient loading into coastal waters may have an inverse relationship with methylmercury availability due to growth dilution from eutrophication, decreases in methylation due to reducing conditions and the binding and sequestration of mercury with organic matter at higher nutrient concentrations. In order to fully understand the relationship between nutrient concentrations and mercury availability, water and sediment samples were collected in 2015 and 2016 in two estuaries and analyzed for mercury and nutrients, with a focus on nitrogen and carbon species. The two study estuaries were chosen to represent a gradient of residential and industrial development. Jamaica Bay is highly urbanized with dense residential and industrial zoning and receives 89% of its nutrient load from wastewater effluent, whereas Great South Bay is characterized largely by residential properties and has a more diverse input of nutrients. Results from 2015 show a stronger relationship between particulate nutrient and mercury concentrations than for dissolved concentrations. Mercury bioavailability appears to decrease with increases in sediment nutrient concentration after an initial increase in mercury bioavailability at very low concentrations. Patterns of coastal mercury will be investigated further with the addition of the 2016 analysis and the relationships will be presented.

RP-146

VOLATILIZATION OF ELEMENTAL MERCURY UNDER ACIDIC CONDITIONS FROM MERCURY- POLLUTED SOIL AND MERCURY WASTEWATER BY A HIGHLY MERCURY RESISTANT IRON-OXIDIZING BACTERIUM ACIDITHIOBACILLUS FERROOXIDANS

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Acidithiobacillus ferrooxidans is an acidophilic chemolithoautotrophic iron-oxidizing bacterium. The bacterium is highly resistant to many kinds of heavy metal ions, but sensitive to Hg2+. Mercury is toxic to almost all organisms because it has a strong affinity for the thiol groups in protein. It is expected that A. ferrooxidans resistant to mercury can be used as a powerful agent for bioremediation of mercury under acidic conditions. A number of heterotrophs have a mercury reductase that reduces Hg2+ with NADPH and generates elemental mercury (Hg0) under neutrophilic pH. In this work, we tried to isolate a mercury resistant A. ferrooxidans.

Of 100 strains of iron-oxidizing bacteria isolated, A. ferrooxidans SUG2-2 was the most resistant to HgCl2 and could grow in an iron medium (pH 2.5) with 6 μM HgCl2. In contrast, a mercury sensitive A. ferrooxidans AP19-3 could not grow on the medium with 0.7 μM Hg2+. When incubated for 3 h in 20 ml of salt solution (pH 2.5) with 0.7μM Hg2+ and SUG 2-2 or AP19-3 cells (1.0 mg protein), 20% and 1.7% of the total mercury added were volatilized, respectively. When SUG 2-2 cells (0.01 mg protein) was incubated for 10 d at 30°C in 20 ml of sulfuric acid (pH 2.5) with ferrous sulfate (2.2 mmol) and 1 g of mercury-polluted soil (7.5 nmol Hg), 4.1 nmol of Hg0 was volatilized. Further addition of ferrous sulfate (2.2 mmol) and SUG 2-2 cells (0.01 mg) to the reaction mixture, with an additional 30 d incubation, increased the amount of Hg0 volatilized to 6.9 nmol. When 50 μl of an acidic-mercury wastewater containing 17.5 nmol of Hg, which is usually produced in the course of everyday laboratory work in Okayama University (pH, 0.98 and COD, 600 mg/L), was incubated in 20 ml sulfuric acid (pH 2.5) with ferrous sulfate (100 μmol) and SUG cells (0.05 mg protein) for 10 d at 30°C, 47% of the total mercury in the reaction mixture (8.23 nmol Hg0) was volatilized.

However, when organic compounds in the mercury wastewater were decomposed by Fenton's method and then treated with SUG cells, 17.5 nmol of Hg (100% of the total mercury in the wastewater) was volatilized. It was found that cytochrome oxidase on the plasma membrane of A. ferrooxidans SUG 2-2 plays a crucial role in the rapid reduction of Hg2+ with ferrous iron to produce Hg0.

RP-148

ENVIRONMENTAL MERCURY STATUS AND TRENDS IN MICHIGAN, USA - A COMPREHENSIVE UPDATE OF ENVIRONMENTAL MERCURY RELEASES, USAGE AND LEVELS IN AIR, SEDIMENTS & WILDLIFE

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Anthropogenic environmental mercury contamination in Michigan dates back over one hundred years to the mining activities in Michigans Upper Peninsula and in the 1970s, massive mercury discharges to the waters of Michigans Lower Peninsula were identified. More recently, atmospheric sources of mercury were characterized as the leading source of loadings to state waters. Significant progress has been made in the state towards reducing all uses and environmental releases of mercury including water discharges, air emissions, biosolids and product use. However, the environmental media and bioindicator data do not necessarily demonstrate consistent temporal trend reductions. The mercury use and release trend data will be presented along with temporal environmental trends and an assessment for successful phase out of use within the state of Michigan. A Michigan state-wide goal is being established that limits atmospheric emissions and deposition, thereby reducing the mercury available for methylation and bioaccumulation in fish. However, further national and international efforts are needed to reduce these impacts because most of the atmospheric mercury deposition in Michigan originates from beyond the states borders.

RP-149

IS THERE MERCURY CONTAMINATION IN DAN RIVER (NORTH CAROLINA/VIRGINIA) DUE TO COAL ASH SPILL IN FEBRUARY 2014?

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Coal ash is the left over material after coal is burned and contains various kinds of toxic metals including mercury (Hg). On February 2, 2014, massive amounts of coal ash and contaminated water from a decommissioned coal-fired power plant spilled into the Dan River near Eden, North Carolina, representing the third worst coal ash spill in the history of the United States. Although analyses on water samples immediately after the incident indicated very low levels of contaminants, including Hg, it is widely speculated that these contaminants would deposit in the bottom sediment where biogeochemical transformations, such as Hg methylation, can occur. Therefore, it is necessary to assess whether there is Hg contamination in the Dan River sediment and biota at downstream sites following the coal ash spill. In July 2015, about 17 months after the spill, we performed longitudinal sampling in 10 sites along Dan River, with 3 sites in the upstream section (up to 3.6 km) and 7 sites in the downstream section (up to 65 km) relative to the spill site. At each sampling site, we collected river channel coarse sand and finer depositional sediments along the shore. We also collected Asian clams (Corbicula fluminea) when available. We analyzed total Hg (THg) for the sediment samples, and THg and methyl-Hg (MeHg) for the clam tissue. Overall, THg in sediment samples was generally considered low but variable, from 2 to 76 ng/g. Sediment THg correlated well with organic matter (OM) content, and thus we normalized sediment THg to OM; OM-normalized sediment THg ranged from 293 to 741 ng/g OM. OM-normalized sediment THg in the upstream section ranged from 319 to 661 ng/g OM. If we assumed that the sediment sample with the highest THg in the upstream section was the upper limit of Hg in Dan River sediment without coal ash, the majority of downstream sediment samples (90%) would have OM-normalized THg lower than this threshold. In fact, the few samples exceeding this upper limit had OM-normalized THg only slightly higher than this upper limit. Clam tissue THg and MeHg levels were variable among sites but did not appear to be different between upstream and downstream sections. Thus, our findings indicated essentially no Hg contamination in Dan River up to 65 km of downstream of Eden, North Carolina due to the coal ash spill after almost 1.5 years of the incident. However, it may be possible that Hg contamination hotspots were either not sampled (e.g., spatially too variable, or buried in deeper layers) or occurred further downstream of our most downstream sampling site (65 km).

RP-150

FLUVIAL TRANSPORT OF MERCURY FROM TWO BURNED WATERSHEDS IN NORTHERN CALIFORNIA

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Due to global climate warming, the frequency and intensity of wildfires are expected to increase in the next few decades. This is especially important in regions with prolonged dry summers, such as in the Mediterranean climate of California where forests have accumulated a large fuel load over the past century. Wildfires are known to release substantial amounts of previously sequestered mercury (Hg) in natural

forests but residual pools of Hg may be left behind in the ash layer and burned soils. These residual Hg pools can be mobilized by intensive rainfall events leading to Hg transport dissolved in surface runoff and attached to eroded soil particles. This study examined the fluvial transport of total Hg (THg) and methyl Hg (MeHg) in two streams in northern California whose watersheds were previously burned in summer 2015: Cold Creek burned by the Wragg Fire (33 km2) and Cache Creek partly burned by the Rocky Fire (281 km2). Event and baseflow water samples were collected in these two streams during the first wet season (January to April, 2016) after the wildfires, and samples were analyzed for THg and MeHg in both unfiltered and filtered samples, as well as for total suspended solids (TSS) and dissolved organic carbon (DOC). Remarkably, stream water from the burned watersheds had extremely high TSS levels, approaching 20 g/L in Cold Creek compared to a maximum of ~50 mg/L in an adjacent unburned reference stream. We observed highly variable unfiltered THg in streams from both burned watersheds, ranging from 0.9 ng/L (baseflow) to 1,379 ng/L (event) for Cold Creek and from 3.8 ng/L (baseflow) to 688 ng/L (event) for Cache Creek. We observed much higher particulate THg during the first or second flush due to the extensive mobilization of surface ash and soil layers by erosion. For filtered samples, we observed only small variations of filtered THg among event and baseflow samples (i.e., 0.81 to 5.6 ng/L for Cold Creek and 1.6 to 15.0 ng/L for Cache Creek), and most of these variations can be explained by differences in DOC concentrations. MeHg levels were low across all water samples but we observed higher MeHg levels and % MeHg in water and particulates at the beginning of the rainy season.

RP-151

EXTREME FLOODING-INDUCED FLUVIAL EXPORT OF TOTAL MERCURY AND METHYLMERCURY IN THE COASTAL PLAIN

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It is widely predicted that global climate change would cause extensive changes in weather patterns, one of which would result in higher frequency of extreme weather events such as hurricanes and droughts. In two consecutive years, two strong hurricanes (Hurricane Joaquin in October, 2015, and Hurricane Matthew in October, 2016) affected much of the Southeastern United States. These extreme weather events caused extensive flooding in the low-lying coastal plain of the southeastern region where wetlands are widespread and representing substantial sources of mercury (Hg) to the freshwater and coastal environment. In this work, we assessed filtered total Hg (THg) and methyl-Hg (MeHg) concentrations in a blackwater river (Waccamaw River) in South Carolina, in which the river drains much of forested wetlands and swamps in the region and represents a model system to examine the impacts of these extreme flooding on fluvial export of THg and MeHg over time. Overall, river discharge increased by about 5-10 times during and right after the surging hydrograph in both years and the flooding lasted for about 2-3 weeks. In fall 2015, we found that dissolved organic carbon (DOC) and THg were both lower than under normal conditions (up to 50% lower). Different from THg, MeHg was much lower during the high flow period and the aqueous concentrations of MeHg were about 5-10 times lower than low flow period, suggesting different biogeochemical controls on the fluvial export of inorganic Hg vs. MeHg. Percentage of total Hg as MeHg (%MeHg) increased from 4% during high flow period to about 25% during low flow period, implying exports of MeHg from those wetlands and possibly some new production of MeHg in the system. Overall, during the high flow period THg flux would be about 2-3 times higher than normal conditions but MeHg flux would be somewhat similar between high and low flow period. Sample analyses are still on-going for 2016 samples and the data will be presented, compared with 2015 data, and discussed in the context of extreme flooding events and biogeochemical Hg cycling in the coastal plain.

2i: Regional and local scale stable isotope studies of mercury biogeochemical cycling and bioaccumulation

RP-152

DRIVERS OF SPATIAL AND TEMPORAL VARIABILITY OF MERCURY AND METHYLMERCURY ACROSS THE EVERGLADES NATIONAL PARK (USA)

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Elevated mercury (Hg) levels in the aquatic food web of the Everglades has been a public concern since the late 1980s, and remains a persistent issue confronting ecosystem restoration efforts. The formation of methylmercury (MeHg) in the system is driven by the bioavailability of inorganic Hg(II) and the metabolic activity of sulfate-reducing bacteria. These in turn are influenced by the abundance and character of dissolved organic carbon (DOC) and sulfate concentrations. Here, we report on an eight-year collaboration between the U.S. Geological Survey and the National Park Service to examine the drivers of spatial and temporal variability of Hg and MeHg within the Everglades National Park. Surface water and forage fish (Gambusia Holbrooki and Jewel Cichlid) were collected annually at 76 sites from 2008 to 2016. Water samples were analyzed for total mercury (HgT), MeHg, DOC, specific UV absorbance at 254 nm (SUVA), and major ions. Fish were analyzed for HgT, MeHg, and stable isotopes of carbon, and nitrogen. In addition, archived fish samples are currently being analyzed for stable isotopes of mercury to provide greater insight into trophic transfer.

Methylmercury concentrations in water and fish exhibited distinct regional patterns with peak levels in the Shark River Slough (SRS) a receiving area for sulfate and DOC-rich canal water. Throughout the SRS, HgT was a strong predictor of MeHg concentrations in filtered water (R-squared = 0.70), whereas in marsh sites unaffected by the canal this result does not hold true (R-squared = 0.15). Regression analysis using a gradient boosting algorithm revealed several additional drivers of MeHg production which included: dry days preceding sampling, sulfate concentration, and SUVA levels (all of which were greatly enhanced in the marsh relative to the SRS). Annual hydrologic conditions were an important driver of mercury levels in water each year. High water during an El Nio event (2009-10) corresponded to a decrease in HgT and MeHg concentrations, while low water levels during a strong La Nia event (2011-12) corresponded to a dramatic increase in concentrations due to drying and rewetting cycles.

Overall, trends of Hg in fish generally followed those of MeHg in filtered surface water with the exception of elevated Hg in fish from the marsh in 2010 (likely due to fish escaping the SRS in high water). In addition, the prevalence of exotic Jewel Fish in the Everglades has greatly expanded over the course of this study; recent data (2010-2013) show that Jewel Fish mercury concentrations (measured as HgT) are 15-20% higher than mercury concentrations in native Gambusia. Mercury sources and diet differences between Jewel Fish and Gambusia will be assessed using stable isotope techniques (Hg, C, N) to better understand their mercury uptake dynamics.

RP-153

TRACKING SOURCES OF MERCURY IN THE IDRIJA MINING AREA – THE RELATIONSHIP BETWEEN MERCURY ISOTOPES AND SPECIES IN SOILS, SUSPENDED MATTER AND SEDIMENTS

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Mercury (Hg) released by mining activities can be highly dispersed in the environment and may undergo species transformations processes, which are essential to evaluate environmental risk. Hg from roaster emissions or mining-residues is accumulated in soils and sediments. In aquatic systems Hg can be transported over great distances as dissolved organic matter complexes or bound to suspended matter (SM). Hg-isotope analysis have been used to track Hg-sources in Hg-mining areas although it is mostly unclear to which extent changes in Hg-isotope ratios are attributed to different sources or Hg-species transformations. In Idrija-Slovenia, Hg was mined as Hg-sulphide (cinnabar-ore, α-HgS) for centuries. Dumping of mining-residues caused accumulation of cinnabar in river sediments, whereas atmospheric Hg deposition led to contamination of soils and enrichment of organically-bound Hg, which, in contrast to cinnabar, can potentially be methylated in aquatic systems. Hg released from soils and mine dumps is mainly transported via SM in Idrijca river to the Gulf of Trieste (GT) in Italy. So far, high δ^{202}Hg values in the marine environment were related to cinnabar from the Idrija mine, and different values from that of cinnabar where assigned to the Adriatic background, but organically-bound Hg derived from soils have been neglected. Here, we determine Hg-species and Hg-isotopes in SM, soils and sediments from the Idrijca-catchment to decipher variability of Hg-isotope ratios related to distribution of Hg-species. Hg-isotopes were determined by means of MC-ICP-MS while Hg-species were analyzed using Hg-thermo-desorption.

In general, δ^{202}Hg values in SM correspond to those found in soils ranging from -2.81 to 0.73‰ and from -2.45 to 0.15‰, respectively. Speciation measurements in different grain sizes reveal that smaller grain sizes (0.45-20 µm) are dominated by organically-bound Hg, while larger grain sizes mainly contain cinnabar (>20 µm). Samples dominated by cinnabar show relatively higher δ^{202}Hg values (~50% cinnabar, δ^{202}Hg > -1.01‰) while organically-bound Hg shows lower δ^{202}Hg values.

Hg-isotopic ratios combined with speciation analyses reveal that most Hg in SM transported to GT is soil derived organically-bound Hg. During rain events SM-loads in the river drastically increase, and also the portion of cinnabar in SM increases due to erosion of larger particles from soils and mining-residues. Our results indicate that the polluted soils in the wider Idrija area are the most important source of Hg transported to GT, and that this Hg organically-bound Hg forms have a large potential for methylation and uptake in the marine food web.

RP-155

ASSESSMENT OF MERCURY POLLUTION IN SOUTHWEST BALTIC SEA AS A RESULT OF HISTORICAL USE OF AIR DEFENCE AMMUNITION COMBINING HG SPECIATION AND ISOTOPIC COMPOSITION

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In the region of Kiel Bay (Dnisch-Niendorf), Southwest Baltic Sea, more than 1.2 million Hg-containing anti-aircraft grenades were shot from World War II artillery training grounds. The majority of these shells exploded in the air, spreading their Hg content. Meanwhile, an unknown proportion of these shells did not explode and ended up on the seafloor, which bear the potential of future Hg-releases into the marine environment. The condition of the unexploded grenades and their potential for Hg release are still unknown, and the current distribution of Hg and its species in waters, sediments and organisms in this sector of the Southwest Baltic Sea is unclear.

The quantification of Hg and its species is an essential tool to evaluate regional environmental pollution. More recently Hg isotopic composition has been widely applied in tracing Hg contamination sources, biogeochemical processes and metabolic fates in environment and living organisms. Sediments act as an important sink for anthropogenic Hg pollution. The polluted sediments exhibited Hg isotopic compositions of anthropogenic and background contributions, whose isotopic composition can be differentiated. Furthermore, despite sediments represent the main Hg source to the surrounding food web, the last one displays a different Hg isotopic signature according to the trophic position and foraging depth of the organism. Such variation of Hg isotopic composition values between biota and their nearby sediments are suggested to be related to biogeochemical processes (e.g. methylation/demethylation) and other environmental factors in each specific system. Therefore, a better comprehension of the biogeochemical fate of the Hg species is needed in such Hg impacted ecosystem.

In this work, Hg concentration, speciation (GC-ICP-MS) and isotopic composition (CVG-MC-ICP-MS) is determined in marine surface sediments and aquatic organisms along the food web, including benthic organisms, plankton and fish that were collected in the ammunition affected area. The main objective of this work is to estimate the Hg contamination extent from the anti-aircraft munitions site to the target living organisms and potential Hg biogeochemical pathways before its introducing into the food web.

RP-156

INSIGHTS FROM THE SPATIAL AND TEMPORAL DISTRIBUTIONS OF MERCURY SPECIES AND ISOTOPES IN BIVALVES FROM THE FRENCH COASTLINE

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Mercury cycles between atmosphere, terrestrial and aquatic reservoirs through a complex combination of transport and transformation processes, until it is buried in oceanic or terrestrial sediments. Monomethylmercury is the main species bioaccumulated and bioamplified in the food chain. Knowledge of the origin (continental, oceanic or local sediment) of this species for the littoral environnment can still be improved.

This study focuses on ~.200 samples of bivalves (mussels: Mytilus edulis and Mytilus galloprovincialis and oysters: Crassostrea gigas and Isognomon alatus) from ~80 stations along the French coast. The goals of this study were i) to describe Hg levels, speciation and isotopic composition in various bioindicator bivalves from the French coastline, and ii) to identify possible geographic, taxonomic or temporal variations in these properties.

In the bivalves, we observed that the variations in methylmercury concentrations follow linearly those of total mercury (HgT). Preliminary results of isotopic fractionation of HgT in some of the samples do show regional effects and allow to differentiate English channel,. Atlantic, and Mediterranean coastlines. These differences may come from the various trophic regimes revealed by NC stable isotopes, from different fractionnation by the three biological species of bivalves, from different mercury source isotopic signatures, or both.

At most of the study sites, HgT concentrations have not decreased since 1987, despite regulations to abate or ban mercury used by anthropic activities.

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RP-157

MERCURY ISOTOPE FRACTIONATION DURING DARK REDUCTION IN SATURATED EAST FORK POPLAR CREEK SOIL

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Riparian soils and sediments of the East Fork Poplar Creek (EFPC) floodplain (Oak Ridge, TN) contain large quantities of mercury from up-gradient contamination at the Y-12 National Security Complex. Important questions remain, however, on the long-term fate of legacy mercury in soils and sediments at this location. A recent study by our group observed substantial dissolved gaseous mercury (Hg(0)) evolution in saturated soil from the EFPC floodplain that contains mercury predominantly as nanoparticulate mercuric sulfide. This finding challenges the notion that authigenic mercuric sulfide is an environmental sink for mercury under all conditions. Periodic soil flooding could lead to the recycling of legacy mercury to the atmosphere. We use stable mercury isotope measurements to (1) provide insights on the process(es) responsible for the formation of Hg(0) in laboratory saturation experiments and (2) quantify the isotopic signature of mercury emitted from the EFPC floodplain to the atmosphere. A comparison of laboratory and field measurements allowed us to evaluate the environmental significance of dark Hg(II) reduction on the fate of legacy mercury in soils.

The stable mercury isotope composition of pore water samples (n = 22) from microcosm experiments was quantified over 36 days of flooding; previous work showed that the reduction of divalent mercury (Hg(II)) to Hg(0) controls mercury release dynamics. We also quantified the stable mercury isotope composition of the soil prior to the start of the experiment (t = 0 day; n = 3) and throughout the progression of the

36 day experiment (n = 6). As flooding proceeded, substantial mass-dependent fractionation (MDF) of stable mercury isotopes was observed resulting in pore water signatures becoming progressively lighter (δ202Hg = -0.52 to -1.70‰) and soil signatures progressively heavier (δ202Hg = +0.15 to +0.75‰). Mass-independent fractionation (MIF) of odd-mass isotopes in pore waters was also observed (Δ199Hg = +0.03 to +0.23). We employed a binary mixing model to explain the processes responsible for MDF and MIF of pore water and soil mercury using two endmembers: (1) the soil mercury at t = 0 day and (2) Hg(0) formed through dark Hg(II) reduction. In the field, stable mercury isotope compositions were quantified on atmospheric samples collected by gold amalgamation above the EFPC floodplain (n = 6). Stable mercury isotope measurements of atmospheric samples are compared with results from the laboratory experiments and previous investigations of the contamination site, and are discussed in context of the fate of mercury in the EFPC floodplain.

RP-158

TRACKING MERCURY AND ITS STABLE ISOTOPES IN SEDIMENTS OF THE HACKENSACK RIVER ESTUARY

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Estuarine sediments accumulate mercury (Hg) from watershed runoff and industrial point sources. However, the resuspension and transport of sediments by estuarine, tidal, and storm surge associated mixing can redistribute Hg far from where it was originally deposited. As a result, identifying the sources of Hg in complex urbanized estuaries, is challenging. Here we use Hg stable isotopes to identify the sources of Hg in sediments within the Hackensack River estuary, a tributary to the lower Hudson River estuary in New York and New Jersey, USA. Concentrations of total Hg (>99% inorganic Hg) in sediment from the Hackensack River estuary varied from 0.06 to 154 ug g-1 with the highest concentrations measured in sediment from upper Berrys Creek estuary just below the West Riser tide gate (86 ug g-1) and upper Peach Island Creek (55 ug g-1). The mean d202Hg value of mercury from Berrys Creek estuary and two small tributaries, Peach Island Creek and Ackermans Creek, was significantly higher ($p < 0.001$) than that from the main stem Hackensack River and its tributary Bellmans Creek. The spatial distribution of mercury and its stable isotopes indicates that mercury from Berrys Creek and its tributaries mixes with, and is partially diluted by mercury from a lower concentration source that is more depleted in 202Hg (lower d202Hg values) as it enters the Hackensack River. Mixing plots of d202Hg vs. inverse total Hg concentration in sediment for the entire system show that d202Hg values decline linearly with decreasing Hg concentrations. Using a binary mixing model, it is estimated that most (>75%) of the mercury in Bellmans Creek and perhaps Mill Creek originated from upper Berrys Creek. Surface sediments from Peach Island Creek had very high mercury concentrations indicating that they could be an important source of mercury to the system.

RP-159

USING MERCURY STABLE ISOTOPES IN FISH TO IDENTIFY BIOAVAILABLE MERCURY IN A CONTAMINATED ESTUARY

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Tracking the sources and accumulation of mercury in coastal marine fish remains a challenge. While the isotopic composition of mercury in fish varies among species and ecosystems reflecting differences in diet as well as the extents and mechanisms of mercury transformations in the environment, it is not easily connected to feeding habitats or bioavailable pools of mercury within a single ecosystem. In order to build on previous work that explored the utility of mercury stable isotopes in the identification of bioavailable mercury in aquatic ecosystems, we estimated δ202Hg values of bioavailable total mercury (THg) and methylmercury (MeHg) prior to their accumulation in the food webs that lead to killifish (Fundulus heteroclitus) and white perch (Morone americana) in the mercury-contaminated Hackensack River estuary, New Jersey, USA. Among four spatially distinct and two developmentally defined populations of these fish, MeHg concentrations were not correlated with those in sediment or suspended particulate matter. Average mass-dependent mercury isotope ratios (δ202Hg) in the fish varied from -0.38‰ to +0.55‰, and fish from all six populations accumulated mercury with positive Δ199Hg and Δ201Hg values, which are produced by the mass-independent fractionation (MIF) of mercury stable isotopes. δ202Hg values of bioavailable THg and MeHg were estimated using the extents of MIF in fish to account for photochemical transformations of inorganic mercury and MeHg, and were strongly dependent on the percent of THg in fish present as MeHg (%MeHg), which varied from 30% to 100%. Estimated δ202Hg values of bioavailable MeHg for two spatially distinct populations of killifish were -0.28‰ and +0.30‰, which are similar to directly measured δ202Hg values for MeHg in sediments from the environments in which each population lived (-0.19‰ and +0.40‰, respectively). However, estimated δ202Hg values of bioavailable MeHg for adult and juvenile white perch (0.48 to 0.87‰) were higher than that for MeHg in sediments throughout the Hackensack River estuary (-0.4 to +0.4‰). This likely reflects the diverse diet and wide feeding range of migratory white perch which may consume prey with isotopically heavier MeHg within or outside of the Hackensack River. These results demonstrate that mercury stable isotopes can be used to identify local scale sources of mercury in fish living in complex environments and have the potential to be used to identify distinct populations of estuarine forage fish and as a proxy for their feeding locations.

RP-160

SOURCE ASSESSMENT OF MERCURY CONTAMINATION ALONG THE GRAND PORTAGE TRAIL, MN (USA)

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The 14-km Grand Portage Trail (GRPO), located in extreme northeastern Minnesota, was a primary route of transport between Lake Superior and inland waters for the French-Canadian Voyageur fur trade during the 17th-19th centuries. Recent work has indicated elevated levels of total mercury, methylmercury, and % methylmercury in components of the lower food web (water, sediment, soil, benthic invertebrates), compared to other national parks in the western Laurentian Great Lakes region. Surficial soil and sediment samples at GRPO yielded 3 to 4-fold enrichment in total Hg relative to organic matter content when compared to other regional forested sites. We sampled soil cores at five locations along the GRPO trail in June 2015 to define the spatial extent of total Hg contamination, and to determine whether the Hg stable isotopic signature differed between contaminated and non-contaminated sites. Two locations (Fort Charlotte and the Stockade) were located at each terminus of the trail, and were known historic locations of vermilion (a bright red HgS-containing pigment) storage and use. These terminal sites exhibited total Hg concentrations (Ft. Charlotte: 6.5±5.0 μg/g dw; Stockade: 0.58±0.36 μg/g) far exceeding locations between them along the trail (0.052±0.021 μg/g). Analysis of the Hg stable isotopes 199Hg and 202Hg by multi-collector ICP-MS indicated that the contaminated sites were indeed isotopically similar to each other (Ft. Charlotte and Stockade data combined: δ202Hg(II): -0.49±0.14‰, Δ199Hg(II): 0.00±0.03 ‰), but different from both the low-total Hg locations mid-trail (δ202Hg(II): -1.24±0.17 ‰, Δ199Hg(II): -0.15±0.07 ‰) and reference soils collected at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada (δ202Hg(II): -1.67±0.17 ‰, Δ199Hg(II): -0.24±0.07 ‰). Samples formed a mixing line between the contaminated and non-contaminated sites, with the mid-trail sites falling between the GRPO contaminated sites and that of ELA. Two archived vermilion samples from the fur trade era were analyzed isotopically for comparison, one each from GRPO and Fort Michilimackinac (Mackinaw City, MI). The GRPO vermilion exhibited an isotopic signature that was markedly similar to the GRPO contaminated sites, while the Michilimackinac sample did not. Our results suggest that anthropogenic contamination associated with historic fur trade commerce is likely responsible for elevated total and methylmercury concentrations observed in the contemporary GRPO food web. We plan to analyze additional regional archived vermilion samples to aid in source attribution.

RP-162

TRACING ATMOSPHERIC MERCURY FROM MARINE BOUNDARY LAYER IN THE YELLOW SEA AND BOHAI SEA USING STABLE MERCURY ISOTOPES

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Source apportionments of mercury (Hg) using stable Hg isotopes have been applied in many previous studies, providing unique clues of typical emission sources and processes in the environmental circulation of Hg. However the fingerprint of atmospheric Hg isotopes, especially in the background area, has been rarely investigated limited by the extremely low concentrations and complicated transformation among three species of atmospheric Hg (gaseous elemental Hg, gaseous oxidized Hg and particle-bound Hg). In this study, total gaseous Hg (TGM, composed by gaseous elemental Hg and gaseous oxidized Hg) samples were collected using chlorized active carbon trap in marine boundary layer of the Yellow Sea and Bohai Sea in summer, 2016. Negative δ202Hg (-1.26±0.69‰, 1σ, n = 7) and Δ199Hg (-0.09±0.05‰, 1σ, n = 7) signatures were observed in TGM samples collected in the Yellow Sea, and samples collected in the Bohai Sea shows more negative δ202Hg (-2.02±0.69‰, 1σ, n = 9) and near-zero Δ199Hg (-0.02±0.04‰, 1σ, n = 9) signatures. The isotopic compositions and ratio of Δ199Hg to Δ201Hg (~1.0) suggesting different mixing ratio of gaseous Hg from both natural background pool and anthropogenic emissions transported from continent, with influences from environmental processes, i.e. the photochemical reactions and evaporation of Hg in the marine surface. In addition, negative Δ200Hg signatures (-0.04±0.03‰, 1σ, n = 7) observed in TGM samples collected in the Yellow Sea implying the active oxidation of elemental Hg and adsorption/desorption on the particle surface.

2k: Mercury in the oil and gas industry, from initial exploration through production to end-of-life decommissioning

RP-163

MERCURY IN BLACK SHALES OF THE LATE DEVONIAN-EARLY MISSISSIPPIAN BAKKEN FORMATION

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The concentration of Hg in black shales is typically in the range of 10s to 100s of ppb and, in some instances, can exceed 1,000 ppb. This range is similar to that of coal but there is comparatively little information available on the occurrence of Hg in black shales. In this study we

consider the concentration of Hg in black shales of the Late Devonian-Early Mississippian Bakken Formation, North Dakota (USA). The Bakken Formation is a major oil producer, but it is also representative of other North American black shales and thus can provide information on the biogeochemical cycling of Hg in black shales in general.

Mercury concentrations were determined by direct mercury analyzer for 33 samples of the Bakken Formation. Concentrations range from 31 to 395 ppb with the exception of one outlier of 792 ppb that is associated with a pyritic lag deposit. By comparing the concentration of Hg to that of other trace metals (V, Mo, Zn) we infer that most of the Hg in Bakken black shales was derived from normal seawater. There is a positive correlation between the concentration of Hg and both total organic carbon and total sulfur, thus complicating efforts to determine the association of Hg in the black shale. Mercury enrichment in the sulfide lag interval indicates that a significant fraction of Hg is associated with pyrite, consistent with work from the modern ocean demonstrating the pyritization of Hg along with a suite of transition metals (Mo, Zn, Co, and Cu). However, in our sample set, wherever Hg exceeds 200 ppb, it is largely decoupled from total sulfur, indicating a potential role for organic carbon as a host for Hg where its concentrations are highest. In some cases the fraction of Hg associated with organic carbon may exceed that associated with sulfides. Determining the concentration and occurrence of Hg in Bakken shale helps determine its origin and potential mobility during disturbance of this interval for oil and gas production.

RP-164

MERCURY AND METHYLMERCURY IN THE ATHABASCA OIL SANDS REGION OF NORTHERN ALBERTA, CANADA

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Bituminous oil sands in northern Alberta and Saskatchewan (Canada) represent the worlds third largest reserve after Venezuela and Saudi Arabia. Rapid development of these oil sands deposits over the last three decades has raised concern about human health and environmental impacts. Alteration of the mercury cycle is of concern because local peoples have traditionally relied on hunting and fishing for food in this region and Hg consumption advisories exist for walleye in the Athabasca River near major developments and for gull and tern eggs in the Peace-Athabasca Delta, located ~150 km north of the major development area. As part of the Canada-Alberta Joint Oil Sands Monitoring program, we have been examining sources of mercury to the oil sands region, including atmospheric deposition potentially originating from bitumen upgrading facilities and fugitive dust from sources such as open pit mines, and leakage of tailings ponds, which are waste water storage dykes. To quantify atmospheric deposition to the region, we have been utilizing dated lake sediment cores and annual sampling of the springtime snowpack at sites located varying distances from the major development since 2012. Our measurements demonstrate that aerial loadings of numerous organic and inorganic contaminants, including total and methylmercury, increase with proximity to the major developments exhibiting a bulls-eye pattern on the landscape. To determine if methyl mercury is produced within snowpacks or deposited directly in that form, potential rates of methylmercury production in snowpacks and melted snow were quantified in 2015 using mercury stable isotope tracer experiments. At the four sites examined, methylation rate constants were low in snowpacks (km=0.0010.004 /d) and non-detectable in melted snow, except at one site (km=0.0007 /d), suggesting that in situ production is unlikely an important source of methyl mercury to oil sands region snowpacks. To determine the impacts of snowmelt on aquatic ecosystems, we also measured total and methyl mercury in five tributaries that have varying degrees of development on their catchments at a high frequency over the ice-free season in 2012-2014. Results to date suggest that while total mercury loads are tightly linked with hydrologic discharge and proximity to developments and bitumen deposits, methyl mercury loads increase in late summer when methylation activity is likely highest. Currently, we are coupling snowpack and river measurements and using a GIS approach to tease apart natural from anthropogenic sources to these rivers. Preliminary data from tailings ponds sampling will also be presented.

RP-165

MERCURY AND METHYLMERCURY IN TAILINGS PONDS OF THE ATHABASCA OIL SANDS REGION, ALBERTA, CANADA

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There are currently about 170 billion barrels of economically recoverable oil in the Athabasca Oil Sands Region (AOSR), ranking Canada as the world's largest bitumen reserve and third largest oil reserve following Saudi Arabia and Venezuela. During extraction and processing, 0.5 to 4.0 barrels of sodium-rich water for each barrel of oil are produced. This sodium-rich water and slurry, referred to as tailings, are released in great volumes (1 million m^3/day) as waste into dykes referred to as tailings ponds. To date, several studies have demonstrated the presence of toxic compounds in tailings water, including volatile organic compounds, polycyclic aromatic hydrocarbons, and naphthenic acids. With no previous studies (to the best of our knowledge) examining mercury concentration in tailings ponds, four ponds were sampled for concentrations of total mercury and methylmercury. Samples were collected from surface waters, water columns, and bottom sediment samples at Horizon, the only pond at Canadian Natural Resources Ltd., and three ponds at Syncrude Canada Ltd. (Southwest In-pit, Mildred

Lake Settling Basin, and Southwest Sand Storage). Total mercury concentrations in water samples were low overall, ranging from 0.16 - 0.57 ng/L. Southwest In-pit was noticeably lower than all other ponds with an average mercury concentration of 0.21 ± 0.04 ng/L, while the other ponds had concentrations >0.30 ng/L. Sediment mercury concentrations at Horizon and Southwest in pit were low at 31.4 ± 0.83 and 39.2 ± 1.88 ng/g, respectively. At MLSB, sediment samples marginally exceeded the Threshold Effect Level for freshwater set by Canadian Council of Ministers of the Environment (130 ng/g), with average concentration of 134 ± 69.1 ng/g. Methylmercury concentrations in water samples were also quite low (0.01 – 0.08 ng/L) at all ponds with the exception of Mildred Lake (0.41 ± 0.11 ng/L). Methylmercury in sediments at both Horizon and SWIP were quite low (0.15 ± 0.06 ng/L). Mildred Lake, however, had sediment methylmercury concentrations 3x higher (0.46 ± 0.04 ng/L), which is still within background levels. Due to high particle content and complex matrices, depth profile samples could only be analyzed in Southwest In-pit, which showed no evidence of changing mercury or methylmercury concentrations with depth. As a result of these analytical issues, further studies are recommended for water column analysis, primarily at Mildred Lake Settling Basin.

RP-166

MERCURY DETERMINATION IN SUBSEA PIPELINE FOR DECOMMISSIONING MANAGEMENT

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It is generally known that mercury is a naturally occurring element associated with oil and gas fields in the Pacific Rim region, particularly in the Gulf of Thailand. Petroleum products sourced from this region contain plenty of mercury resulting in decomposition on the metal surfaces, and finally complicated management both at offshore platform and at onshore treatment facilities. At the time of decommissioning, subsea pipeline management could be either leave in place or transport to onshore disposal facilities. Leaving in place is a preferred option due to engineering and cost attractiveness. However, one of key concerns of this option is to ensure the idle pipelines to be left in situ must be clean enough so that residuals will not cause any significant impacts to marine biota. Qualitative and quantitative analysis of the Hg contaminant were performed on both scale and bulk of the pipeline using several diagnostic techniques including energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF) and inductively coupled plasma spectrometry (ICP). The XRD spectra of the scale surface indicated the existing forms of mercury in the pipeline as Hg0, HgCl2, Hg2Cl2, HgS, and HgSe. Relative elemental concentration for each element of interest was visualized using EDS but limited by the low detection limits of approximately 1000 ppm. It was also found that XRF was not appropriate for Hg quantitation especially in the carbon steel matrix with high roughness and irregularity. Analytical procedure and validation was developed and established based on the ICP technique so that the Hg level within the pipeline sample could be accurately obtained. The ICP results confirmed that mercury existed only on surface and scale, and did not penetrate into bulk. Moreover, the mercury contaminant was inhomogeneously distributed over the representative scale samples. Highly corroded surface caused by pipeline leak was liable to have high level of mercury contaminated.

RP-167

SPATIAL AND TEMPORAL PATTERNS OF MERCURY IN FISH IN THE ATHABASCA OIL SANDS REGION AND IN RELATION TO DEPOSITION TRENDS (ALBERTA, CANADA)

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The Fort McMurray area in Alberta, Canada, is rich in bitumen with oil sands mining beginning in the late 1960s and expanding exponentially in recent decades. These operations have been controversial given the size and extent of the open pit mines and tailings ponds located along a ca. 75 km stretch of the Athabasca River. The Athabasca Delta and western Lake Athabasca (WLA), ca. 130 km downstream, support significant fisheries and wildlife populations. Among the many concerns expressed with oil sands activities is the enhanced release of mercury (Hg) into the environment from emissions, the disturbed landscape, seepages, etc. potentially affecting Hg concentrations in fish; an early study reported increased Hg in Walleye from the Athabasca River based on three years of sampling over 1976-2005. Subsequent expanded studies conducted under the Joint Oil Sands Monitoring Program are providing enhanced understandings of the influence of oil sands activities on Hg in the environment. Here we present highlights of these studies with a special interest in fish.

Hg emissions from the oil sands industry increased from ca 20 kg/yr in the late 1990s to reach 135 kg in 2010 with a subsequent decline; these releases were relatively small when compared to the ca. 600 kg/yr Hg release by coal-fired power plants (Wabamun Lake area) to the south. Hg deposition to the snowpack was primarily in particulate form and highest (1,000 ng/m2) close to the developments. In contrast, Hg concentrations were highest (ca. 100-200 ng/g) in lake sediments more than 50 km distant from the development and lowest (ca. 50-70 ng/g) at sites closest to the developments; concentrations were similar to lakes in the Northwest Territories ((NWT). While Hg concentrations in sediment cores have been increasing since the 1800s, peak concentrations were reached in the early 2000s and have been declining in recent years.

Hg concentrations in Walleye and Lake Whitefish from the Athabasca River and in Lake Trout, Walleye, Northern Pike and Burbot from WLA remained relatively stable and at historic levels. Hg concentrations in predatory fish tend to exceed 0.5 g/g as fish reach 10 years of age as also has been observed in small to medium size lakes in the NWT. Spatial variations in fish Hg concentration are primarily relatable to fish size, age, diet; lake size; and differences between lake and river systems. Concentrations are similar to those observed in fish from similar habitats in the NWT.

RP-168

LOSSES OF MERCURY FROM HYDROCARBON SAMPLES WHEN SAMPLING INTO INERT COATED STAINLESS STEEL CYLINDERS (INCLUDES HYDROCARBON GASES AND PRESSURISED HYDROCARBON LIQUIDS)

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Mercury is a naturally occuring contaminant found in almost all oil and gas reservoirs, existing in a range of concentrations and in a number of different forms.

Processing of gas and oil that is rich in mercury can be problematic and needs to be monitored and managed on an ongoing basis. The three main issues resulting from the presence of mercury are:

- Liquid Metal Embrittlement (LME) [a type of corrosion]
- Catalytic poisoning (an issue for downstream refining processes)
- Environmental issues (includes worker exposure and release to the environment)

For these reasons accurate quantification of mercury in produced gas and oil is essential. Ideally, determination of mercury in gases, condensates and oils should be carried out at source (at the well site or processing facility). Due to the volatile nature of mercury and its affinity to adsorb onto various sample vessels, transportation and subsequent delays between sampling and analysis is not advised.

It is possible to purchase inert coated stainless steel sampling equipment and cylinders (most commonly these are based on a thin surface silica chemistry based layer). The inert coating helps to minimise losses of mercury but it does not eliminate losses. This presentation highlights the extent of the losses that can be encountered when utilising inert coated sampling equipment and demonstrates the importance of analysing samples as soon as possible after sampling.

A theory for the mechanism of loss of mercury within an inert coated sampling cylinder is also put forward.

RP-170

EFFECTIVE REMOVAL OF MERCURY FROM CRUDES AND CONDENSATES USING MERCAWAY(SM) PROCESS TECHNOLOGY

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MERCAWAY(SM) process technology is a straightforward and commercially proven process for reducing mercury (Hg) content in crude oil and condensate using easily understood chemistry and well-proven unit operations. There are four key steps in the MERCAWAY(SM) processing scheme as follows: 1) Desanding to remove sand and other particles, 2) Reaction to convert mercury to filterable particulate HgS, 3) Filtration to separate HgS particles from treated crude/condensate stream, and 4) Polishing to adsorb most of the remaining mercury after the filtration step.

In this presentation, we will describe an application of MERCAWAY(SM) in the Oil and Gas industry. In this application, greater than 98% of the mercury was removed to produce a condensate with less than 50 ppb Hg. The process disposes the high mercury filter cake generated in this process by slurrying it with produced water and injecting back undergrounded in a closed system. This approach minimizes potential exposure to operation and maintenance personnel.

RP-172

MERCURY DECONTAMINATION IN THE OIL AND GAS INDUSTRY

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Onshore, offshore, mercury has been part of the oil and gas process for many years. With mercury levels found across the world dealing with contaminated products can be unique to every situation. In the upstream markets mercury can be higher in end of life reservoirs, dealing with contamination has changed to accommodate this. With tighter country oil and gas markets downstream and storage have also been affected to some degree and methods specifically adapted to each process, area and service stream executed. Upstream and downstream within the oil and gas market, increased contamination comes increased risk. There are safe and efficient ways in dealing with possible exposure and dealing with mercury. Hygiene and personnel safety is put at risk during maintenance and shutdown/turnaround areas, which lead to major health concerns and legalities throughout operational life. Methods, equipment and chemistry have all been specially adapted to dealing with mercury and successful processes in removing mercury from the work environment. This dialogue investigates mercury decontamination technologies and how specialised processes have worked across the industry under specific country and client standards. The specific, specialised and unique chemistry processes and equipment used for each individual case.

RP-173

MERCURY WASTES FROM THE OIL AND GAS INDUSTRY: TECHNOLOGIES INVOLVED IN THE TREATMENT AND FATE OF THE RECOVERED MERCURY

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The operators of oil and gas fields containing mercury have to deal with a wide scope of mercury contaminated wastes, including but not limited to PPE, sludge, various liquids and mercury adsorbents. The mercury appears in various forms and the concentrations range from a few tens of ppm to several percent.

The treatment, respectively the recycling, of materials with such a wide variety of physical and chemical characteristics implies adapted technologies to decontaminate the waste itself but also to treat the off gas generated.

A special focus will be given to the technology for the recycling of Hg adsorbents (Hg guard beds, activated carbon) and the challenges linked to the recycling of this waste stream.

The mercury recovered from the wastes also represents a great challenge. Whilst some uses for high purity mercury still exist, these are restricted and therefore a safe and sustainable disposal route for the mercury is a growing demand, especially for companies with a high corporate responsibility.

4d: Technologies and approaches for mitigating mercury emissions

RP-175

SULFURIZED BLACK CARBON SORBENTS FOR MERCURY VAPOR CAPTURE IN LOW-RESOURCE SETTINGS

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Mercury (Hg) is a hazardous atmospheric pollutant released during fossil fuel combustion and small-scale gold mining. While impregnated activated carbon sorbents are well studied for Hg vapor capture in developed countries and large industrialized settings, there exist no suitable low cost alternatives for Hg capture from artisanal and small-scale gold mining (ASGM) in developing countries. This research seeks to develop an easy-to-manufacture carbon sorbent using elemental sulfur and activated carbon or hardwood-based biochar for potential use during ASGM Hg-amalgam heating. Consumer-grade sulfur powder was melted on granular activated carbon or hardwood biochar in a process feasible for a cook stove setting. Activated carbon and biochar were successfully sulfurized to more than 5% sulfur by weight. The products were tested for sorption of gaseous Hg(0) (500 µg Hg per cubic meter) in an air gas stream at 23°C. The sulfurized activated carbon achieved higher Hg(0) adsorption capacity (7800 mg/kg) relative to unsulfurized activated carbon (680 mg/kg) and sulfurized biochar (2400 mg/kg). Sorption isotherms were determined to discern Hg(0) sorption mechanisms, and indicated the process could be modeled as a pseudo-first order process. Analysis of surface speciation of sulfur and Hg by X-ray spectroscopy techniques revealed that these elements were bound in a mercury-sulfide-like structure in a single plane but were not in the form of highly crystalline structures. This research demonstrates a novel and effective Hg(0) sorbent using consumer-grade materials and synthesis equipment and provides an option for improved Hg vapor reduction for individuals located in resource-limited settings such as ASGM sites.

RP-176

DEVELOPMENT OF SCR CATALYST REGENERATION PROCESS FOR ENHANCED MERCURY OXIDATION

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The removal of mercury from flue gas in wet scrubbers is greatly increased if the flue gas mercury (Hg) is present as a water-soluble oxidized species (e.g. Hg2+). Increased mercury oxidation upstream of wet scrubbers improve overall mercury removal with minimum additional costs. The selective catalytic reduction (SCR) catalyst in a fossil fuel power plant plays a key role as a co-benefit for oxidizing elemental mercury (Hg0). However, there are influencing factors like the ammonia ratio applied for NOx-removal, which reduces the performance of regular SCR catalysts related to mercury oxidation.

Currently the SCR catalyst Original Equipment Manufacturers (OEMs) have provided commercial enhanced mercury oxidation catalysts to the coal-fired power plants for reducing stack Hg emission. To the SCR catalyst regeneration industry, developing enhanced Hg oxidation regenerated catalyst is important to help power plants further cost savings on NOx and Hg removal. The different proprietary methods have been studied, optimized and applied into the catalyst regeneration process for further improving Hg oxidation. A systematic study in a laboratory micro reactor has been performed to evaluate SCR catalyst mercury oxidation. The test results demonstrated that STEAG SCR-Tech's Hg oxidation regeneration methods performed as well as commercial new enhanced Hg oxidation catalyst. Furthermore, regular deactivated

SCR catalyst was converted to enhanced Hg oxidation catalyst by means of the SCR catalyst regeneration process.

RP-179

SIMULTANEOUS REMOVAL OF NO AND HG0 FROM COAL-COMBUSTION FLUE GASES USING RICE HUSK SIO2 MODIFIED BY COPPER RECYCLED FROM INDUSTRIAL WASTE.

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Mercury (Hg) and NOx discharged from coal-fired power plants (CFPPs) have both received special concern owing to the high toxicity and long retention time in the environment of Hg and the formation of acid rain, photocatalytic smog and secondary PM2.5 from NOx. In this research, rice husk derived SiO2 impregnated by copper recycled from industrial waste was tested under a simulated flus gas condition for simultaneous removal of NO and Hg. CuOx of 10, 25, and 50 wt% was impregnated onto the rice husk derived SiO2. The BET result showed that the presence of CuOx increased the surface area as compared to the raw SiO2. 50 wt% CuOx/SiO2 having the highest BET surface area may lead to its best Hg and NO removal efficiency. Surface-treated catalysts were analyzed with XRD; however, there is no significant peak at high angle of 35.8° and 38.2° among all the samples, indicating that CuOx was highly dispersed on the surface, which can enhance the contact with the pollutants and lead to a greater conversion in catalytic oxidation of Hg0 and reduction of NO.

CuOx/SiO2 showed great NO removal efficiency between 200 and 400°C under the tested condition. 50% CuOx/SiO2 can achieve more than 60% NO removal efficiency under a broad operation temperature (250-400°C). The CuOx-modified SiO2 showed excellent Hg removal ability under 150°C. These results indicate that using rice husk derived SiO2 impregnated with copper recycled from industrial waste can be a feasible way for multipollutant control of Hg and NOx.

RP-180

PILOT-SCALE CAPTURE OF MERCURY, ARSENIC, AND SELENIUM FROM WARM SYNGAS AT ELEVATED PRESSURES BY PALLADIUM SORBENTS

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Warm gas cleanup of fuel gas from integrated gasification combined cycle power plants is important in order to preserve both their higher thermal efficiencies and to eliminate dirty water circulation and treatment systems. Ten pilot-scale tests of palladium on alumina sorbents for the removal of trace contaminants from several types of coal-derived syngas at elevated temperatures and pressures were conducted at the Southern Company National Carbon Capture Center. Between 96 – 100% removal of mercury, arsenic, and selenium from all syngas types, sour and sweet, was observed at 500 °F and elevated pressures of 150 – 200 psig. The results indicate that the Pd sorbents exhibit large capacities for the capture of Hg, Se, and As under varying conditions and over extended test periods. Current preliminary work also shows that the sorbent is not only regenerable, but that the sorbent is just as effective at capturing these contaminants after regeneration. Future work and tests will focus on use of lower loadings of Pd, higher syngas flow rates, and further regeneration cycles in the removal of the trace contaminants, as well as the possible removal of other contaminants.

RP-183

CONTROL OF MERCURY EMISSIONS – ALTERNATIVE METHODS

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With implementation of the EPA Mercury Air Toxics Standard (MATS) in the United States, electric generating units (EGUs) are required to achieve high levels of mercury reduction (excess 90% in most cases). While activated carbon is widely utilized to reduce mercury emissions to meet the MATS regulation, it often results in high operational costs and significant maintenance expense. With mercury emission limits approaching in the European Union, it is important to recognize alternative methods that utilize existing capital equipment to minimize mercury control impacts. Nalcos MerControl Technologies reduce mercury emissions via liquid based reagents, reducing operational costs and greatly increasing ease of application. Nalcos presentation will provide full-scale results achieved with novel MerControl technologies; including MerControl 8034 Plus (designed for wFGDs) and MerControl SD-Hg (designed for semi-dry scrubbers).

RP-184

MERCURY REMOVAL FROM WASTE INCINERATION FLUE GAS: HETEROGENEOUS OXIDATION AND CAPTURE BY WASTE-DERIVED FLY ASHES

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Among all heavy metals, mercury (Hg) is a pollutant of special concern due to its major impact on human health and the environment.

Incineration is one of the main waste management strategies used for the treatment of municipal solid waste (MSW), some which, consist of Hg-containing wastes, such as batteries, paint residues, thermometers, thermostats, light switches and others products which are discarded as household waste in MSW. Removal of Hg from MSW incineration flue gas is essential from the stand point of environmental pollution control. After incineration, all mercury content in waste is released as Hg0 which passes into the flue gas and is gradually oxidized (mainly into HgCl2 form), by both homogeneous and heterogeneous reactions. Some degree of Hg removal can be achieved by existing conventional air pollution control devices (APCDs), normally used to control NOx, SO2, and particulate matter. Hg bound to particles (Hgp) is usually the easiest species to be removed from flue gas as a co-benefit in existing emission control devices, such as fabric filters (FFs) or electrostatic precipitators (ESPs). Some Hg interaction/retention mechanisms have already been proposed in fly ashes from coal-fired power plants, however, fewer studies are still available concerned about fly ashes from MSW incineration. It must be taken into account that conditions of both processes are different, and therefore, the composition and characteristics of the resulting fly ashes cannot be always comparable. In this study, several samples of fly ashes (characterized by composition, surface area and carbon content) derived from MSW incineration were assessed for mercury removal under MSW incineration conditions at laboratory scale, using a fixed-bed quartz reactor packed with fly ash. The results obtained showed that unburned content, composition of flue gas (e.g. HCl and SO2 content) and operating temperature are important variables controlling capture of mercury. Fly ash enriched in unburned carbon can both, oxidize Hg0 and capture it effectively in presence of chloride. Surface area together with carbon content of fly ash and content of HCl in flue gas were correlated with the oxidation and adsorption of elemental mercury. The results obtained in this study may help to propose the interaction mechanism and to understand the fate/behavior of mercury in a baghouse, and provide a deeper knowledge of the impacts on fly ash properties in waste incineration.

RP-185

COST EFFECTIVE REDUCTION OF MERCURY USING POWDER ACTIVATED CARBON INJECTION

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With more than a decade of user experience at a variety of utility scale coal-fired power plants, powder activated carbon has been thoroughly demonstrated as a powerful tool for the reduction of mercury emissions. Nevertheless, in the past sorbent usage costs required to sufficiently reduce mercury emissions could be prohibitively high due to a variety of factors negatively impacting the efficiency of the activated carbon sorbent. Such factors include Air Quality Control System (AQCS) configuration, fuel type, and the presence of Flue Gas Conditioning (FGC) with SO3. An additional factor which can significantly increase the required sorbent usage rate is the application of Dry Sorbent Injection (DSI) for acid gas (i.e. HCl, SO2) control. With previous generations of sorbent products a combination of these factors could often drive up sorbent usage costs required to meet emissions compliance to the point of being economically unfeasible. In response, new generations of powder activated carbon sorbentsdemonstrating significantly increased mercury removal efficiency and tolerance to DSI have been recently developed. This increased mercury removal efficiency and DSI tolerance has not only allowed a substantial reduction in sorbent usage costs required to meet mercury emissions compliance under both the Mercury and Air Toxics Standards (MATS) and Canadian provincial regulations, but can also reduce compliance costs globally. As demonstrated in both full-scale field trials and long-term usage at standard operating conditions, this represents a significant cost savings to the electric utility.

RP-187

A ZIRCONIUM-BASED METAL ORGANIC FRAMEWORK-CARBON HYBRID SORBENT FOR MERCURY AND OXYANIONIC HEAVY METAL REMOVAL

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Adsorption using highly porous and highly functionalized sorbents is a straightforward removal technology currently being employed in wastewater treatment. Metal-organic frameworks are materials that have been gaining popularity in remediation technology due to their high surface areas, high specificity towards certain pollutants, as well as high structural integrity. Zirconium-based MOF, UiO66, has been shown to remove oxyanionic metal pollutants in water such as selenite, however, this study found out that it has low affinity for mercury. A novel sorbent was synthesized from activated carbon and UiO66 MOF via solvothermal method to remove both mercury and oxyanionic metals from aqueous solutions. The composite was characterized using FSEM-EDS, FT-IR, XRD, and TGA, and showed successful integration of the UiO66 and activated carbon components. The sorbent has a SBET of 1051 m2 g-1. Batch adsorption tests using CV-AFS and ion-chromatography reveal that the Hg 2+ and SeO3 2- uptake of the hybrid follows the pseudo-second order kinetics with observed Qmax values and rate constants of 249.9 mg g-1, k = 5.6E-05 and 177.2 mg g-1, k = 3.16E-05, respectively. The presence of equal concentrations of As, Cr, and Se does not significantly affect the adsorption performance of the hybrid for mercury. There was no definite effect of pH on Hg 2+ adsorption but a decrease in SeO3 2- uptake was observed at pH values higher than 7. The hybrid is a viable sorbent for both anionic and cationic heavy metal contaminants.

RP-189

REMOVAL OF HG0 FROM SIMULATED COAL-FIRED FLUE GAS BY MN SUPPORTED MONTMORILLONTE

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As one of the most important anthropogenic sources of mercury emission, coal combustion brings a large amount of Hg0 into the atmosphere. However, Hg0 removal is particularly difficult due to its low water solubility and high vapor pressure. And the widely application of activated carbon injection technology is limited for its high operation cost and poor capacity. Thus, it is of great significance to develop novel materials that are highly-efficient, low-cost and environmental-friendly.

In this study, natural montmorillonite (MK10) and Mn were used as support and active component, respectively. One the one hand, its Hg0 removal performance was compared with catalysts such as Mn/TiO2, Mn/Al2O3 and Mn/SiO2. Various characterizations (BET, XRD, TEM, XPS, H2-TPR and Hg-TPD) were conducted to analyze the interaction mechanism between active component and different supports. On the other hand, the effects of preparation methods, loading values, temperatures and gas components for Hg0 removal on Mn/MK10 were investigated. The Hg0 removal mechanism was discussed, on the basis of characterization results.

Hg0 removal efficiencies of four kinds of catalyst were evaluated and compared (Mn/MK10 > Mn/SiO2 > Mn/TiO2 > Mn/Al2O3), and different characterization were conducted to explain the proposed mechanism. Physical adsorption dominated Hg0 removal for Mn/Al2O3 and Mn/SiO2 at low temperature (150C), while chemical adsorption was more important at high temperature (350C). Chemical adsorption and oxidation played the main role for Mn/TiO2 and Mn/MK10, respectively. Besides, the effect of MnOx morphologies for Hg0 removal was investigated. Amorphous MnO2 benefited Hg0 oxidation most, amorphous Mn2O3 partly oxidized Hg0 at high temperature, and crystalline MnO2 basically promoted the chemical adsorption.

The Hg0 oxidation mechanisms of Mn/MK10 in different atmosphere were studied. NO had a promoting effect due to the formation of NO2 and Hg(NO3)2. The addition of only 5 ppm HCl led to excellent Hg0 removal performance as HCl enhanced Hg0 conversion to HgClx. The inhibition effects of SO2 and H2O(g) were ascribed to the formation of MnSO4 and the competitive adsorption, respectively. Moreover, Hg0 removal performance was maintained at 80%99% (NO/SO2=0.261.71) in simulated flue gas without HCl, which appeared to be promising in industrial application.

RP-191

EXPERIMENTAL STUDY ON HG2+ REDUCTION AND RE-EMISSION IN THE WET FLUE GAS DESULFURIZATION SYSTEM

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Wet flue gas desulfurization (WFGD) system has benefit Hg2+ pollution control performance in coal fired power plant. However, Hg2+ reduction and emission take place in the WFGD system, resulting in Hg0 emission to the atmosphere. In this work, the effects of operating temperatures, pH values and O2 concentration on the reduction of Hg2+ were investigated in the presence of SO32- and SO42-. The effect of SO42-/SO32- ratios were also investigated, since SO42- is considered as an important factor that affect the Hg2+ reduction reaction. The results indicated that Hg0 release was enhanced with the operating temperature increases. When the pH value of the liquid decreased, a remarkable emission process was obtained through the experiments. It is also found that the Hg2+ reduction will be inhibited with high availability of excess SO32- in the occurrence form of Hg(SO3)22-, but lower concentration of SO32- (<2mM) would lead to enhanced mercury re-emission by forming more redox unstable HgSO3. The content of sulfate ion, as well as SO42-/SO32- ratio nearly have no impact on Hg0 emission. In addition, O2 generally inhibited Hg0 emission with complex way. Situations where O2 exists induce a second emission by damage the stable redox complexes between Hg2+ and SO32-. However, as a result of oxidation of oxygen, the emission inhibited subsequently by forming complex HgSO3SO42- , which in turn had a negative effect on Hg0emissioin.

RP-192

THE STUDY ON REMOVING HG0 FROM THE SIMULATED FLUE GAS BY ABANDONED SEMI-COKE DESULFURIZER

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In this paper, the Hg0 removal from the simulated flue gas was investigated by the abandoned semi-coke desulfurizer (DUISC). As contrast samples, the semi-coke sorbents USC and UISC were also prepared by high-pressure impregnation under ultrasound-assistance. The mercury removal performances of the sorbents DUISCUISC and USC were tested in a fixed-bed reactor. The results show that the order of Hg0 removal capacity is DUISC> UISC> USC, and DUISC has the highest mercury capacity of 1.81 μg/g and the longest breakthrough time of 12.5 h. Adsorbing Hg0 is a kind of typical gas-solid reaction, thus the surface of sorbent is the location of the demercuration reaction. From BET results, the specific surface of DUISC is smaller than that of USC. Apparently, the mercury removal performance is also related to the components of sorbent. Compared with USC, the diffraction peak of ZnO can be seen from UISC, and the mercury activity of UISC increases to 1.24 μg/g and it is 2.2 times as high as USC. It is obvious that the existence of ZnO is beneficial to removing Hg0. However for DUISC, the diffraction peak of ZnS is also appeared besides ZnO. In accordance with DUISC's higher mercury capacity, ZnS plays a main role in removing Hg0. The reason is that ZnS can be oxidized to S0, then S0 and Hg0 may react to HgS. So elemental sulfur (S0) formation leads to the best mercury removal performance of DUISC. In a word, the removing mercury of DUISC includes physisorption and chemisorption of Hg0, and the latter is the most important. ZnO and ZnS are active components of DUISC. Meanwhile, -OHC=O and COOH are the main functional groups by FTIR which adsorb and oxidize Hg0.