行政院所屬各機關因公出國人員出國報告書

（出國類別：國際會議）

赴美國參加
2017 全球汞污染國際會議
International Conference on Mercury as a Global Pollutant

服務機關：行政院環境保護署

姓名職稱：呂澄洋科長、徐宏博技士、
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派赴國家：美國

出國時間：106 年 7 月 14 至 23 日

報告日期：106 年 10 月 18 日

摘要

第 13 屆「2017 全球汞污染國際會議(International Conference on Mercury as a Global Pollutant, ICMGP)」於美國羅德島舉行，為期 6 天，共 57 國的環保部門及學術研究人員代表與會，出席人數約 1,000 餘人，希望藉由全球汞監測最新發展及區域性汞污染來源之特徵變化分析，有效管理汞排放，以減少生態系統對汞之暴露。會議內容包含：區域性大氣汞傳輸及沈降-亞太地區汞監測網(Asia-Pacific Mercury Monitoring Network, APMMN)、最新水俣公約(Minamata Convention on Mercury)現況及科學評估，運用先進技術降低汞污染排放、生態汞循環及環境中汞化合物分析技術等多項議題。

本署於鹿林山背景測站架設大氣汞自動連續監測儀器及汞濕沈降採樣器，進行乾、濕沈降之汞監測計畫，並加入全球大氣汞監測網(Atmospheric International Research Monitoring Network, AMNet)及美國國家大氣沈降監測網(National Atmospheric Deposition Program, NADP)，另與美國環保署及 NADP 共同成立「亞太地區汞監測網(APMMN)」，強化亞太地區共同監測機制以及監測資料交換與分享，相關研究成果豐碩。本次會議不但設有 APMMN 海報專區，本署「亞太地區汞監測網及環境監測技術聯合中心」計畫主持人，國立中央大學大氣物理研究所許桂榮副教授亦上台報告，展示鹿林山空氣品質背景測站受汞污染跨洲長程傳輸影響，並藉由國際合作、資料交換，提升我國在國際上之能見度。

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一、 前言

北美事務協調委員會及美國在台協會於 1993 年 6 月 21 日簽訂「駐美國臺北經濟文化代表處與美國在臺協會環境保護技術合作協定」，簡稱「中美環境保護技術合作協定」，執行單位分別為我國行政院環境保護署及美國環保署，自此開啟臺美緊密的環保合作與交流。為延續環保技術合作協定之執行，截至目前為止共簽訂了 11 號執行辦法，第 11 號執行辦合作規劃為 2015 年到 2017 年。

為進一步改善全球環境，加強國際合作，提升我國在全球及區域國際環保的領導地位，拓展夥伴計畫參與國家，本署在美國環保署長吉娜 麥卡馨(Gina McCarthy)女士率團訪臺之際及我國馬總統見證下，魏署長 國彥於 103 年 4 月 14 日宣布成立「國際環境夥伴計畫(International Environment Partnership，IEP)」(如圖 1.1)。

透過臺美環保技術合作協定以及國際環境夥伴計畫之執行，不但建立與美國及其他國家之環保官員及環保專家交流機會，更拓展我國雙邊及區域性環保外交合作。亞太地區汞監測網(Asia-Pacific Mercury Monitoring Network, APMMN)專案，即為國際環境夥伴計畫專案之重點項目之一。

圖 1.1 魏署長宣讀「國際環境夥伴計畫(IEP）」成立聲明

二、 會議背景及目的

汞是全球性污染物，主要經由大氣長程傳輸到達全球各地，透過大氣乾、濕沈降回地表，進入陸域及水域生態系統，再經由食物鏈累積危害人體健康，傷害腦、神經系統及腎臟，更可被微生物轉化為高毒性甲基汞，國際癌症研究中心(The International Agency for Research on Cancer, IARC)已將甲機汞歸類為 2B 致癌物。汞污染對環境影響深遠，逐漸引發各國重視大氣汞污染跨境傳輸的監測課題，故聯合國於 2013 年 10 月 9 日在日本熊本市公開簽署關於汞污染防治的全球性公約：「水俣公約(Minamata Convention on Mercury)」，並於 2017 年 8 月 16 日正式生效。

我國有鑑於汞對環境會來帶來嚴重影響，在 2007 年始建立鹿林山高山背景測站同時，就開始架設大氣汞自動連續監測儀器，由於臺灣位於亞洲氣流系統之下風處，高山背景測站之監測數據因而極具代表性。透過臺美環保技術合作協助，鹿林山測站目前已分別加入全球大氣汞監測網(Atmospheric International Research Monitoring Network, AMNet)及美國國家大氣沈降監測網(National Atmospheric Deposition Program, NADP)，監測技術與世界先進國家同步並獲得認可。2013 年我國環保署、美國環保署及 NADP 共同成立「亞太地區汞監測網(Asia-Pacific Mercury Monitoring Network, APMMN)，與東南亞國家共同合作，拓展區域大氣汞監測，藉以瞭解其環境濃度分布情形，強化國際共同監測機制以及監測資料交換與分享，進而訂定管制策略與控制人為排放量。

本次「全球汞污染國際會議(International Conference on Mercury as a Global Pollutant, ICMGP)」之參與國家有美國、臺灣、日本、義大利、韓國、波蘭、印尼、加拿大、南非等共 57 國的環保部門及學術研究人員代表與會，出席人數 1,000 餘人，會議內容包含：區域性大氣汞傳輸及沈降-亞太地區汞監測網(APMMN)、最新水俣公約現況及科學評估，運用先進技術降低汞污染排放、生態汞循環及環境中汞化合物分析技術等多項議題，希望藉由全球汞監測最新發展及區域性汞污染來源之特徵變化，有效管理汞排放，以減少生態系統對汞之暴露。

三、 會議過程及內容重點整理

本次「全球汞污染國際會議」於 7 月 16 至 21 日在美國羅德島舉行。相關議程如附件 1，主要行程及內容簡如下表：

日期	行　程　內　容
106.7.14-15	啟程，出發至美國羅德島
106.7.16	➢ 國際汞污染座談會 ➢ 各國分享汞污染現況及討論水俁公約
106.7.17	➢ 全球（區域）性汞監測技術及污染管制 ➢ 水俁公約：科學及政策關聯性討論會議 ➢ 區域性大氣汞傳輸及沈降：亞太地區汞監測網(APMMN)
106.7.18	➢ 環境中汞物種流佈、先進汞分析討論會 ➢ 水陸生態（循環）系統中大氣汞沈降
106.7.19	➢ 環境保護討論會議：汞污染對全球氣候變遷影響 ➢ 汞排放量、最新大氣汞沈降模式座談會
106.7.20	➢ 汞對人體及生物毒性、甲基汞生物濃縮性 ➢ 汞污染管制及降低汞排放技術座談會
106.7.21	➢ 汞及其化合物之混合毒性討論會 ➢ 全球及區域性人為汞污染影響座談會
106.7.22-23	返程，回到臺北

圖 3.1 全球汞污染國際會議(ICMGP 2017)海報

第 1 天 (7 月 16 日)

於美國布朗大學(Brown University)進行汞討論會議，包括汞分析品質保證(Quality Assurance)、海水中汞化合物反應及汞生化循環、優化大氣汞量測方法及汞同位素技術應用、評估汞污染場址及生物監測等議題，並就科學角度及政策面研商改善汞污染方式；另於退伍軍人紀念會議廳(Veteran’s Memorial Auditorium)舉辦 ICMGP 開幕儀式，共有 57 國的環保部門及學術研究人員代表與會，並就 71 國已簽署水俣公約(Minamata Convention)進行廣泛討論。

第 2 天 (7 月 17 日)

於美國羅德島會議中心(Rhode Island Convention Center, RICC)進行全球汞污染影響綜合討論，包括大氣汞傳輸及沈降模式分析、環境汞化合物排放及分析、全球汞循環及汞同位素研析排放源、海洋中汞生化循環機制等事項；我國於會議中展示且解說美國環保署與我國共同建構亞太地區汞監測網(Asia-Pacific Mercury Monitoring Network, APMMN)，並以我國為環境監測技術中心，持續協助東南亞國家汞監測樣品分析、數據傳輸及技術交流，可拓展我國與周邊夥伴國的合作。

第 3 天 (7 月 18 日)

於美國羅德島會議中心(RICC)進行汞區域性變化特徵綜合會議，討論議題包括科學方式執行水俣公約、淡水與沿海生態系統中汞來源及循環、人工淘金(Artisanal Small-scale Gold Mining, ASGM)過程中汞排放現況及未來預測、汞處理技術無害化、氣候變遷及土地利用對汞於環境流佈影響。

第 4 天 (7 月 19 日)

於美國羅德島會議中心(RICC)進行汞污染場址評估綜合會議，探討汞源頭排放及土壤汞通量之相關性、評估礦場中汞含量分析、定量廢水中甲基汞濃度、活性碳去除液態汞等先進技術；前美國環保署長 Gina McCarthy 於 RICC 演講「地球的未來：環境保護、汞污染及氣候變遷」，兩度提及我國對亞太地區汞監測之技術貢獻，並與本署出席人員會談美國環保署持續與我國汞監測技術合作。

第 5 天 (7 月 20 日)

於美國羅德島會議中心(RICC)進行科學研析、政策制定與水俣公約之綜合討論，針對高濃度汞排放源彙整、銀奈米複合材及活性碳先進技術減緩汞污染影響、各國大氣汞傳輸模式及趨勢分析等項目交換意見；我國於會議中展示鹿林山空氣品質背景測站受汞污染跨洲長程傳輸影響，並說明該測站亦加入美國大氣沈降計畫(NADP)中大氣汞監測網(AMNet)之空氣品質監測站。

第 6 天 (7 月 21 日)

於美國羅德島會議中心(RICC)討論汞對生態系統影響，並就甲基汞對不同水體物種（浮游生物、魚、蛙等）之生物濃縮性研析及交換意見。

圖 3.2 Rhode Island Convention Center, Providence RI

四、參加會議心得及建議

（一） 本次出國主要目的為代表本署赴美國羅德島出席全球汞污染國際會議，瞭解全球汞監測最新發展，7 月 16 日至 18 日討論全球及區域性汞污染特徵與監測技術、大氣汞傳輸及沈降模式分析、7 月 19 日評估汞污染在環境中流佈、前美國環保署長 Gina McCarthy 對汞監測技術及水俁公約進行演說、7 月 20 日至 21 日探討各國大氣汞傳輸模式及趨勢分析、甲基汞對生態系統影響。另由會場展示攤位獲悉美國推動對牙醫診所汞合金廢棄及排放推動管制措施。

1. 我國持續以先驅採樣(Pilot Study)方式，支援泰國、越南、印尼及韓國採集樣品，委託送至中央大學進行汞分析，並輔導及教育訓練東南亞各委託國建立汞監測技術，待各委託國技術成熟後，定期寄送汞樣品至我國進行品質保證與管制(QA/QC)。此外，藉由我國協助泰國、越南、菲律賓等夥伴國建立汞濕沈降採樣技術，輔導建置汞監測採樣點，可鞏固我國於東亞區域內國家之合作關係，促進國際

環境保護工作之交流合作。

2. 美國環保署甫於 2017 年 7 月 14 日公告一項減少牙醫診所汞合金排放的管制規定，以減少醫療過程中廢棄的汞流入下水道進入污水系統成為水污染。該項規定規範牙醫診所必須使用汞合金分離器，另外並採行 2 項由美國牙醫協會(American Dental Associati on, ADA)建議的最佳管理做法，美國環保署預期該項規定推行後可減少 5.1 噸汞排放污染環境。

3. 挪威航空研究中心及波蘭 AGH(Akademia Górniczo-Hutnicza)科技大學預計於 108 年 9 月 8 日至 13 日於波蘭的克拉科夫市(krakow)舉辦第 14 屆 ICMGP 會議，各國對已簽署之水俣公約執行情形、汞監測先進技術及區域性污染管制方式交換意見。

4. 本次會議參與的國家有美國、臺灣、日本、意大利、韓國、波蘭、印尼、加拿大、南非等共 57 國的環保部門及學術研究人員代表與會，出席人數約 1,000 餘人，進行全球汞監測最新發展之技術交流，研商水俣公約中汞之科學量測及政策管制方法。

（二） 建議事項：

1. 美國環保署與我國規劃擴展 APMMN 期程，並藉由我國成立之環境監測技術聯合中心，積極輔助東南亞國家建立汞濕沈降技術，為提供後續新加入汞監測網之國家所需採樣、分析及訓練等作業，且為建構完整 APMMN 監測網，我國持續以專案計畫委託國內產學機構，並評估夥伴國家對汞濕沈降採樣器材需求數量、逐步建置東亞區域性汞監測站址及相關技術人員之培訓，協助推動 APMMN。

2. 我國建構亞太地區汞監測平臺，可共享東南亞國家之汞監測數據、測站資訊、採樣標準作業程序、會議行程、聯繫方式等項目，並藉由此平臺可掌握汞特徵及變化資訊，進而拓展我國環境監測及檢測產業在東南亞地區商機。

3. 美國環保署新公告對牙醫診所汞合金廢棄及排放管制規定，已含括了醫療過程中汞合金回收設備應用要求，具備減少廢棄排放完備實務規劃，可供我國參考。

附件1、2017 全球汞污染國際會議議程

	SUNDAY JULY 16	MONDAY JULY 17	TUESDAY JULY 18	WEDNESDAY JULY 19	THURSDAY JULY 20	FRIDAY JULY 21
08:00		Registration	Registration	Registration	Registration	Registration
08:30		Plenary Session	Plenary Session	Concurrent Sessions	Plenary Session	Plenary Session
09:00	Workshops (ending at 16:30)					
09:30		Break	Break	Break	Break	Break
10:00		Concurrent Sessions	Concurrent Sessions	Concurrent Sessions	Concurrent Sessions	Concurrent Sessions
10:30						
11:00						
11:30						
12:00		Lunch Break (on your own)	Lunch Break (on your own)	Lunch Break (bagged lunch provided)	Lunch Break (on your own)	Closing Ceremony & Reception
12:30						
13:00	Public Information Session (ending at 15:00)			Tours & Excursions from 14:00-17:00 add: Documentary Screening: *The Islands And The Whales*		
13:30		Poster Session	Poster Session		Poster Session	
14:00	Registration					
14:30		Concurrent Sessions	Concurrent Sessions		Concurrent Sessions	
15:00						

15:30	🟨	🟦	🟦	🟩	🟦	
16:00						
16:30		Poster Session Happy Hour	Poster Session Happy Hour		Poster Session Happy Hour	
17:00						
17:30						
18:00			Celebrating George Aiken Rotunda Room			
18:30				Plenary Session: **Gina McCarthy**, EPA Administrator under President Obama		
19:00	Opening Ceremony					
19:30			**Dine Around Providence** OR **Pawtucket Red Sox Ball Game**			
20:00	**Reception**				**Conference Gala**	
20:30						
21:00						
21:30						
22:00						

Updated: July 15, 2017.

附件 2、研討會相關照片

圖 1、亞太汞監測專案夥伴與前美國環保署署長 Gina McCarthy 合照

圖 2、本署呂澄洋科長與前美國環保署署長 Gina McCarthy 合照

圖 3、前美國環保署署長 Gina McCarthy 感謝臺灣給予之支持，給予一個大大的擁抱

圖 4、亞太汞監測專案夥伴與未來 APMMN 規劃藍圖合影

圖 5、本署呂澄洋科長、中央大學許桂榮教授與各國與會學者合照

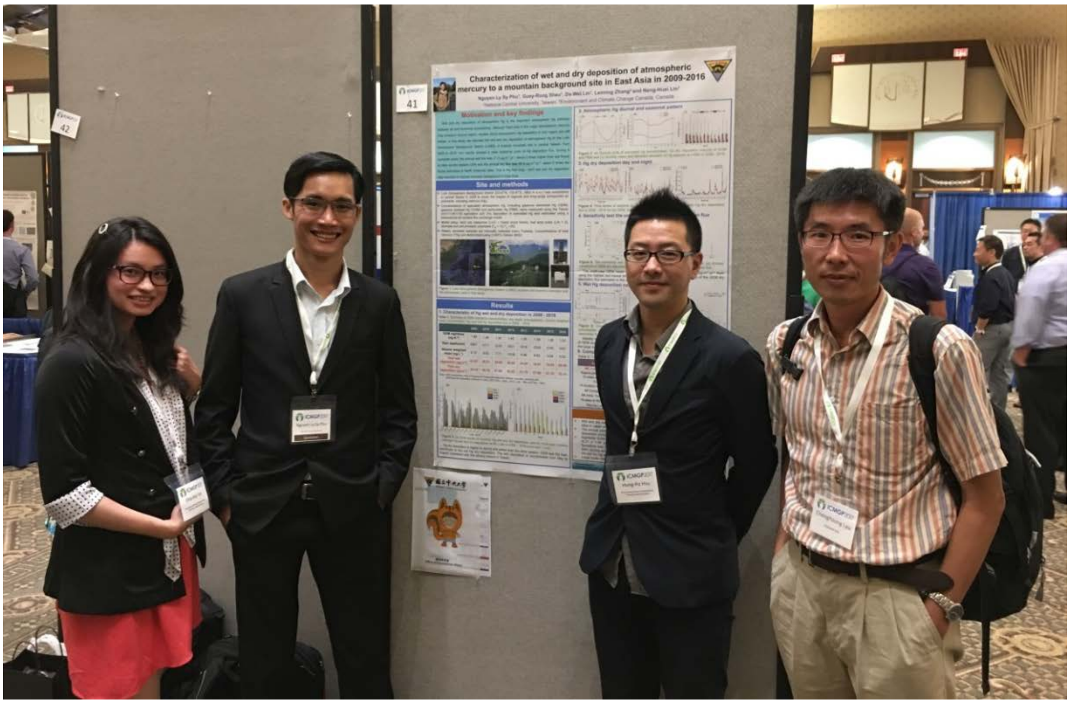

圖 6、本署呂澄洋科長、徐宏博技士、林佳慧技佐與鹿林山背景測站海報合照

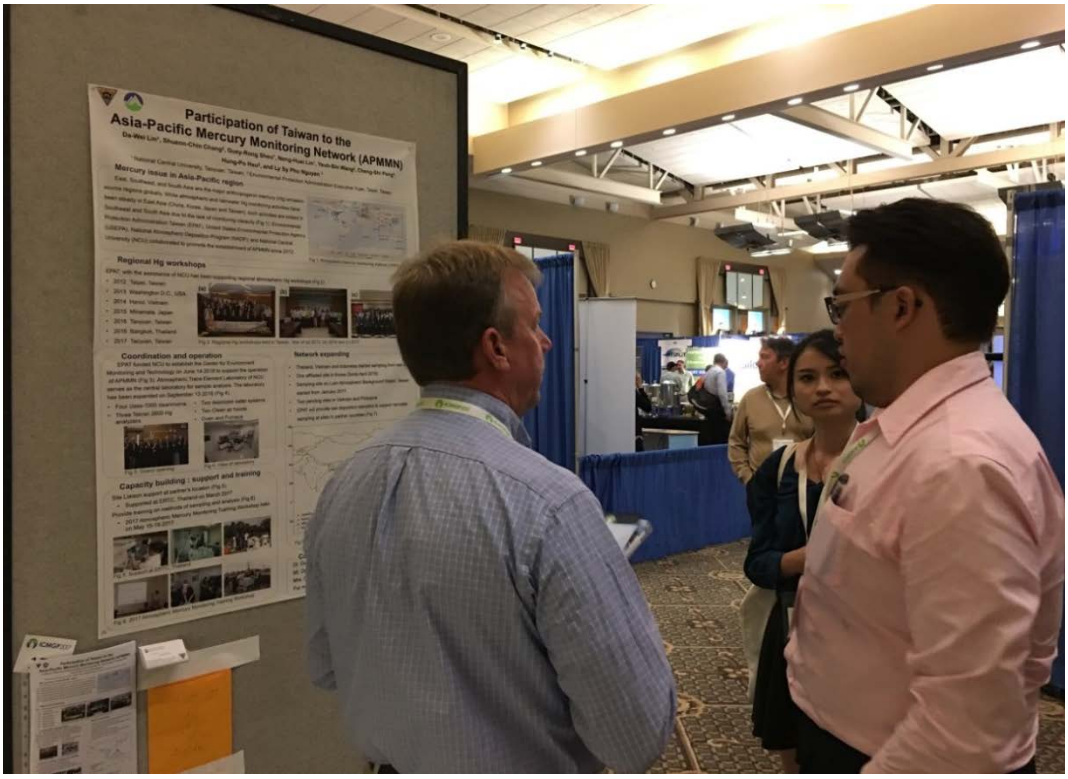

圖 7、美國大氣沈降計畫資深專員 MARK L. Olson 討論 APMMN 發展狀況

Trend and Source-Receptor Relationship of Atmospheric Mercury Observed at a Tropical Mountain Background Site in East Asia in 2006-2016

Guey-Rong Sheu*, Nguyễn Lý Sỹ Phú, Da-Wei Lin, Neng-Huei Lin

Department of Atmospheric Sciences
National Central University
Taoyuan, Taiwan

圖 8、中央大學許桂榮教授發表鹿林山背景測站受汞污染長程傳輸影響

圖 10、「美國國家大氣沈降監測網」將「亞太地區汞監測網」藍圖規畫視為重點展示項目

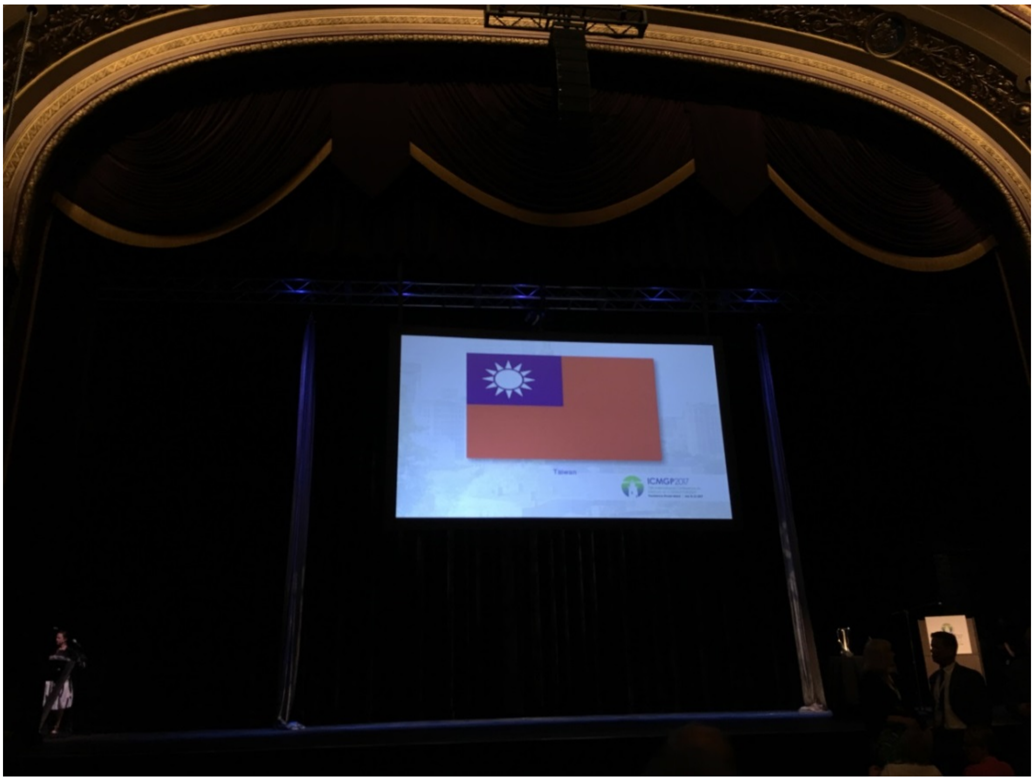

圖 10、ICMGP 年會開幕典禮上投影高掛臺灣國旗

附件 3、會議討論資料

ICMGP2017

Providence, Rhode Island | July 16–21, 2017

13th International Conference on Mercury as a Global Pollutant

Program at a glance

	SUNDAY JULY 16	MONDAY JULY 17	TUESDAY JULY 18	WEDNESDAY JULY 19	THURSDAY JULY 20	FRIDAY JULY 21
08:00		Registration	Registration	Registration	Registration	Registration
08:30		Plenary Session	Plenary Session	Concurrent Session	Plenary Session	Plenary Session
09:00	Open House & Workshops (ending at 16:30)					
09:30		Break	Break	Break	Break	Break
10:00		Concurrent Sessions	Concurrent Sessions	Concurrent Sessions	Concurrent Sessions	Concurrent Sessions
10:30						
11:00						
11:30						
12:00		Lunch	Lunch	Lunch	Lunch	Closing Ceremony & Reception
12:30						
13:00	Public Information Session (ending at 15:00)			Tours & Excursions from 14:00-17:00 Documentary Screening: *The Islands And The Whales*		
13:30		Poster Session	Poster Session		Poster Session	
14:00	Registration					
14:30		Concurrent Sessions	Concurrent Sessions		Concurrent Sessions	
15:00						
15:30						
16:00						
16:30		Poster Session Happy Hour	Poster Session Happy Hour		Poster Session Happy Hour	
17:00						
17:30						
18:00						
18:30				Plenary Session: **Gina McCarthy**, EPA Administrator under President Obama		
19:00	Opening Ceremony					
19:30			**Evening Social Event** (TBC)			
20:00	**Reception**				**Conference Gala**	
20:30						
21:00						
21:30						
22:00						

Updated: July 15, 2017

ICMGP2017
Providence, Rhode Island | July 16–21, 2017

13th International Conference on
Mercury as a Global Pollutant

Overview

Mark your calendars for **July 16–21, 2017** and come join us in Providence, Rhode Island, USA for the **13th International Conference on Mercury as a Global Pollutant**!

Mercury science and management are the focus of attention world-wide, as the complex and multifaceted contaminant drives concerns over human health and wildlife. The Minamata Convention, a global treaty on Mercury, is currently being ratified while local efforts worldwide are in progress to remediate mercury contaminated sites. The theme of this conference will be understanding the multiple factors that accelerate and attenuate recovery of mercury contamination in response to environmental inputs on local to global scales.

> "Integrating Mercury Research and Policy in a Changing World"

The conference and will bring together a diverse community of conference participants, drawing on industry, government, research institutions, NGOs and academics, providing excellent opportunity for collaboration. ICMGP will craft a technical program that reflects the latest advances, highlights critical understanding and promotes active discussion of the science of mercury and innovative strategies for its management.

Providence, one of the oldest and most culturally exciting cities in the United States, is known as *America's Renaissance City*. Providenc is a medium sized city with a charming historical downtown and readily accessible to the Convention Center. This coastal community i home to intriguing restaurants, pubs and coffeehouses. Cultural and recreational opportunities abound, including WaterFire, an environmental art installation that consists of about 100 bonfires that blaze just above the surface of the three rivers that pass throug downtown Providence. Providence is already gearing up to welcome the participants of Mercury 2017.

The conference will be held at the Providence Convention Centre, an engaging venue for Mercury 2017 which can easily accommodat the anticipated number of more than 1000 participants. The Convention Centre is serviced by several international and regional airports, and also accessible by rail from major Northeast U.S Cities.

Please save the date for July 16th – 21st, 2017 and plan to join us in this historic City for this globally-focused conference. Check back t this website regularly for updates or contact our conference organizers at mercury2017@agendamanagers.com with any specific questions.

We look forward to hosting you in 2017!

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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

SLEMR, Franz[1]; EBINGHAUS, Ralf[2]; WEIGELT, Andreas[2]; BRENNINKMEIJER, Carl[1]; RAUTHE-SCHÖCH, Armin[3]; HERMANN, Markus[4]; ZAHN, Andreas[5]; VAN VELTHOVEN, Peter[6]; MARTINSSON, Bengt[7]; ZIEREIS, Helmut[8];
(1) Max-Planck-Institute for Chemistry, Mainz, Germany; (2) Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; (3) Max-Planck-Institue for Chemistry, Mainz, Germany; (4) Leibniz-Institute for Tropospheric Research, Leipzig, Germany; (5) Karlsruhe Institute of Technology, Karlsruhe, Germany; (6) Royal Netherlands Meteorological Institute, de Bilt, the Netherlands; (7) University of Lund, Lund, Sweden; (8) Deutsches Zentrum für Luft-und Raumfahrt, Oberpfaffenhofen, Germany

franz.slemr@mpic.de

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

SHEU, Guey-Rong[1]; NGUYEN, Ly[1]; LIN, Da-Wei[1]; LIN, Neng-Huei[1];
(1) National Central University, Taoyuan, Taiwan

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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

LUKE, Winston[1]; KELLEY, Paul[1]; REN, Xinrong[1]; COHEN, Mark[1]; ARTZ, Richard[1]; OLSON, Mark[2]; SCHMELTZ, David[3]; KOBAYASHI, Nash[4]; COLTON, Aidan[4];
(1) NOAA/Air Resources Laboratory, College Park, MD, USA; (2) Illinois State Water Survey, Champaign, IL, USA; (3) EPA/Clean Air Markets Division, Washington, DC, USA; (4) NOAA/Earth System Research Laboratory, Hilo, HI, USA

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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

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4h: Regional cooperation to track atmospheric mercury transport an deposition: the Asia Pacific Mercury Monitoring Network

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MP-170

ATMOSPHERIC DEPOSITION OF MERCURY SPECIES IN GWANGJU, A RURAL AREA IN SOUTH KOREA

AUTHORS: CHOI, Hyojung [1] ; HAN, Seunghee [1] ;
(1) GIST, Gwangju, South Korea

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.

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MP-171

WET DEPOSITION AND AIR CONCENTRATIONS OF MERCURY AT A RURAL SITE IN THAILAND

AUTHORS: GARIVAIT, Hathairatana [1] ;
(1) Environmental Research and Training Center, Patumthani, THAILAND

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

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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.

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MP-172

NETWORK MONITORING OF MERCURY WET DEPOSITION ACROSS ASIA

AUTHORS: GAY, David [1] ; SHEU, Guey-Rong [2] ; SCHMELTZ, David [3] ; HSU, Hung-Po [4] ;

(1) *National Atmospheric Deposition Program, Champaign, United States;* ***(2)*** *National Central University, Jhong-Li, Taiwan;* ***(3)*** *US Environmental Protection Agency, Washington DC, USA;* ***(4)*** *Taiwan Environmental Protection Administration, Taipei, Taiwan*

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.

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MP-173

CONTINUOUS MONITORING ON ATMOSPHERIC GEM, GOM AND PBM CONCENTRATIONS AND WET HG DEPOSITION FLUXES AT FUKUOKA IN THE NORTHERN KYUSHU OF JAPAN

AUTHORS: MARUMOTO, Kohji [1] ; HATTORI, Tatsuya [2] ; NAGASAKA, Hiromitsu [2] ; SUZUKI, Noriyuki [3] ;
(1) National Institute for Minamata Disease, Minamata, Japan; (2) IDEA Consultants, Inc., Yaizu, Japan; (3) National Institute for Environmental Studies, Tsukuba, Japan

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.

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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

AUTHORS: KIM, Hyuk [1] ; SEOK, Kwang-seol [1] ; KIM, Rok-Ho [1] ; YU, Seok-min [1] ; PARK, Kwang-su [1] ; NOH, Seam [1] ; LEE, Seung-Ha [1] ; KIM, Young-hee [1] ;
(1) National Institute of Environmental Research (NIER), Incheon, Republic of Korea

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.

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MP-176

CONCENTRATIONS AND POSSIBLE SOURCES OF ATMOSPHERIC SPECIATED MERCURY IN A REMOTE ISLAND OF KOREA

AUTHORS: LEE, Soo-Hyun [1] ; HAN, Young-Ji [1] ;
(1) Kangwon National University, Chuncheon, Kangwon, Republic of Korea

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MP-177

PARTICIPATION OF TAIWAN TO THE ASIA-PACIFIC MERCURY MONITORING NETWORK (APMMN)

AUTHORS: LIN, Da-Wei [1] ; CHANG, Shuenn-Chin [2] ; SHEU, Guey-Rong [1] ; LIN, Neng-Huei [1] ; WANG, Yeuh-Bin [2] ;
PENG, Cheng-Shi [2] ; HSU, Hung-Po [2] ; NGUYEN, Ly-Sy -Phu [1] ;
(1) National Central University, Taoyuan, Taiwan; (2) Environmental Protection Administration, Taipei, Taiwan

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).

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MP-178

MERCURY MONITORING IN VIETNAM

AUTHORS: NGUYEN, Thuy [1] ;
(1) Vietnam Centre for Environmental Monitoring , Hanoi, Vietnam

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.

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MP-179

ESTABLISHING STANDARDIZED PROTOCOL FOR ATMOSPHERIC MERCURY NETWORKS WORLDWIDE

AUTHORS: OLSON, Mark [1] ; GAY, David [1] ; SCHMELTZ, David [2] ; GUEY RONG, Sheu [3] ; LIN, Dawei [3] ; LUKE, Winston [4] ;
SUZUKI, Noriyuki [5] ;
(1) National Atmospheric Deposition Program, Champaign, IL, USA; (2) US Environmental Protection Agency, Washington DC, USA; (3) National Central University, Taoyuan City, Taiwan; (4) NOAA Air Resources Laboratory, College Park, MD, USA;
(5) National Institute for Environmental Studies, Tsukuba, Japan

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.

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MP-181

CANADIAN ATMOSPHERIC MERCURY MONITORING: ACHIEVING HIGH QUALITY DATA AND DATA COMPARABILITY

AUTHORS: STEFFEN, Alexandra [1] ; STUPPLE, Geoffrey [1] ; TORDON, Rob [2] ; KEENAN, Rob [2] ; PILOTE, Martin [3] ; SCHILLER, Corinne [4] ; COLE, Amanda [1] ; SKELTON, Greg [5] ;

(1) Environment and Climate Change Canada, Science and Technology Branch, Air Quality Research Division, Toronto, Ontario, Canada; (2) Environment and Climate Change Canada, Dartmouth, Nova Scotia, Canada; (3) Environment and Climate Change Canada, Section Effluents & Eaux usées, Montreal, Quebec, Canada; (4) Environment and Climate Change Canada, Meteorological Services of Canada, Applied Environmental Prediction Science West, Vancouver, British Columbia, Canada; (5) GB Skelton Technical Services Inc, Ontario, Canada

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.

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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.

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Participation of Taiwan to the Asia-Pacific Mercury Monitoring Network (APMMN)

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Mercury issue in Asia-Pacific region

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 (Fig 1). Environmental Protection Administration Taiwan (EPAT), United States Environmental Protection Agency (USEPA), National Atmospheric Deposition Program (NADP), and National Central University (NCU) collaborated to promote the establishment of APMMN since 2012.

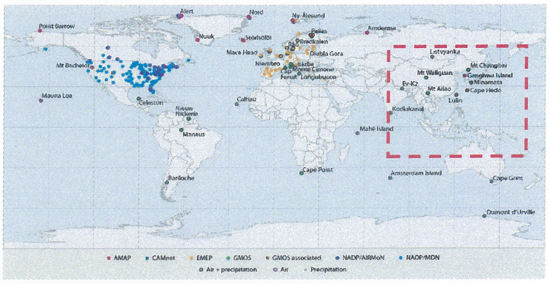

Fig 1. Atmospheric mercury monitoring stations (UNEP, 2013)

Regional Hg workshops

EPAT, with the assistance of NCU has been supporting regional atmospheric Hg workshops (Fig 2).

- 2012 Taipei, Taiwan
- 2013 Washington D.C., USA
- 2014 Hanoi, Vietnam
- 2015 Minamata, Japan
- 2016 Taoyuan, Taiwan
- 2016 Bangkok, Thailand
- 2017 Taoyuan, Taiwan

Fig 2. Regional Hg workshops held in Taiwan. Year of (a) 2012, (b) 2016 and (c) 2017.

Coordination and operation

EPAT funded NCU to establish the Center for Environment Monitoring and Technology on June 14 2016 to support the operation of APMMN (Fig 3). Atmospheric Trace Element Laboratory of NCU serves as the central laboratory for sample analysis. The laboratory has been expanded on September 13 2016 (Fig 4).

- Four class-1000 cleanrooms
- Three Tekran 2600 Hg analyzers
- Two deionized water systems
- Two Clean air hoods
- Oven and Furnace

Fig 3. Grand opening

Fig 4. View of laboratory

Capacity building : support and training

Site Liaison support at partner's location (Fig 5)

- Supported at ERTC, Thailand on March 2017

Provide training on methods of sampling and analysis (Fig 6)

- 2017 Atmospheric Mercury Monitoring Training Workshop held on May 15-19 2017

Fig 5. Support at ERTC, Thailand

Fig 6. 2017 Atmospheric Mercury Monitoring Training Workshop

Network expanding

- Thailand, Vietnam and Indonesia started sampling from late 2014.
- One affiliated site in Korea (Since April 2016)
- Sampling site on Lulin Atmospheric Background Station, Taiwan started from January 2017.
- Two pending sites in Vietnam and Philippine
- EPAT will provide wet deposition samplers to support rainwater sampling at sites in partner countries (Fig 7).

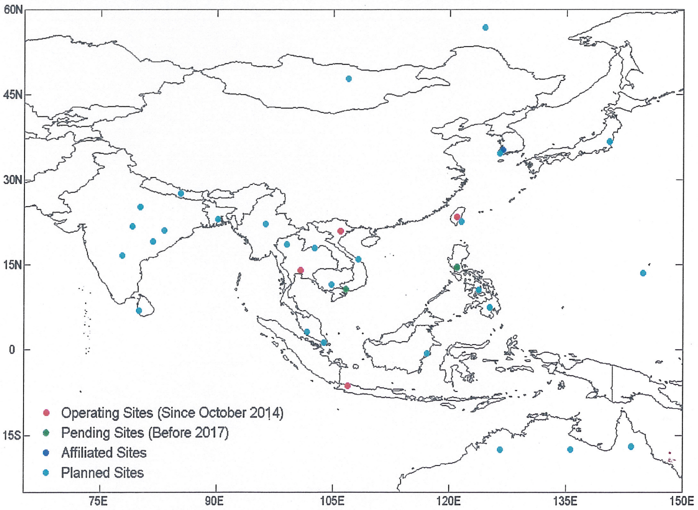

Fig 7. APMMN site status

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For more information, please visit https://apmmn.org

The Asia-Pacific Mercury Monitoring Network (APMMN):

Regional Cooperation to Track the Atmospheric Transport & Deposition of Mercury

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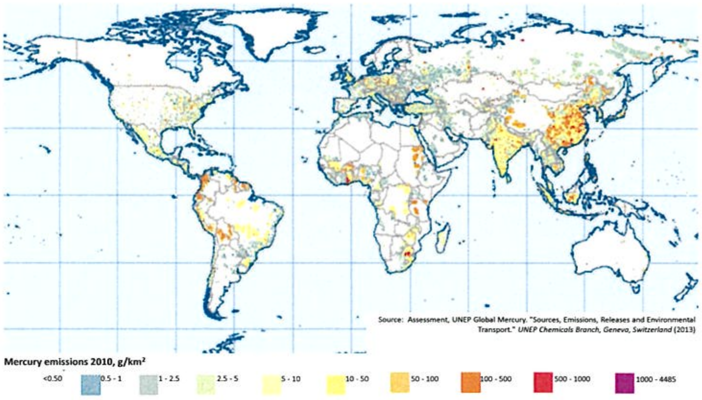
1. Problem

- Increasing industrialization has made Asia the main source region of mercury emissions, with East and Southeast Asia accounting for about 40% of the global total, and South Asia for an additional 8% (Figure 1).
- Anthropogenic mercury emissions data from 1990 to 2005 featured in the 2013 UNEP Global Mercury Assessment suggest increasing trends in Asia, driven by power generation from coal-fired power plants and other industrial activities.
- Mercury emitted to the atmosphere can be transported and deposited locally, regionally, and globally. Once deposited, natural processes convert inorganic mercury to methylmercury (MeHg) – a highly toxic form readily magnified to high concentrations in food webs. Globally, concentrations of MeHg in fish and wildlife routinely exceed dietary thresholds that can harm people and wildlife.

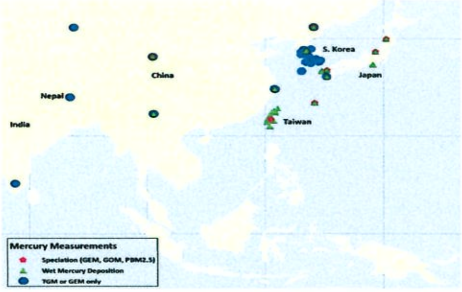


Source: Assessment, UNEP Global Mercury. "Sources, Emissions, Releases and Environmental Transport." *UNEP Chemicals Branch, Geneva, Switzerland* (2013)

Figure 1. Global Distribution of Mercury Emissions from Anthropogenic Sources, 2010

2. Why Do We Need an Asia-Pacific Mercury Monitoring Network?

- Despite the magnitude and extent of Asian mercury emissions, few consistent measurements in the region; no background measurements in Southeast Asia.
- Current monitoring coverage is insufficient to detect spatial and temporal changes in atmospheric mercury and validate regional and global-scale mercury models (Figure 2).
- Consistent, long-term measurements are a first step to determine the magnitude of the problem and to assess the effectiveness of mercury reductions (e.g., Minamata Convention).

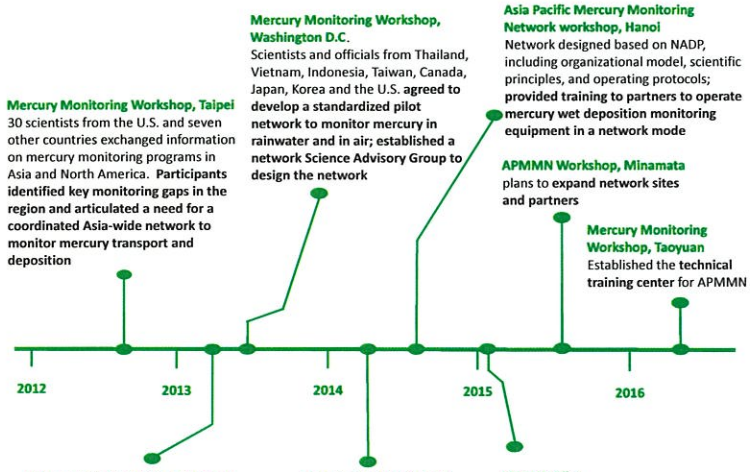


Current measurements made across the region are not networked.

- Non-standardized protocols for field and laboratory operations
- Unknown and inconsistent QA
- Data reside in different locations and typically unavailable

Figure 2. Atmospheric Mercury Measurements in East/Southeast Asia

3. Developing a Scientific Basis for APMMN: Timeline of Progress



Mercury Monitoring Workshop, Taipei
30 scientists from the U.S. and seven other countries exchanged information on mercury monitoring programs in Asia and North America. **Participants identified key monitoring gaps in the region and articulated a need for a coordinated Asia-wide network to monitor mercury transport and deposition**

Minamata Convention on Mercury
established to protect human health and the environment; includes **provisions for research and monitoring to evaluate Convention effectiveness**

Mercury Monitoring Workshop, Washington D.C.
Scientists and officials from Thailand, Vietnam, Indonesia, Taiwan, Canada, Japan, Korea and the U.S. **agreed to develop a standardized pilot network to monitor mercury in rainwater and in air; established a network Science Advisory Group to design the network**

SOPs to monitor mercury in rainwater **developed and adopted by APMMN**

Asia Pacific Mercury Monitoring Network workshop, Hanoi
Network designed based on NADP, including organizational model, scientific principles, and operating protocols; **provided training to partners to operate mercury wet deposition monitoring equipment in a network mode**

APMMN Pilot
Two mercury wet deposition operate in Thailand and Vietnam; pending sites in Korea Philippines, and Indonesia (Figure 3)

APMMN Workshop, Minamata
plans to **expand network sites and partners**

Mercury Monitoring Workshop, Taoyuan
Established the **technical training center** for APMMN

4. Network Goal and Objectives

- **Goal:** Systematically monitor wet deposition and atmospheric concentrations of mercury in a network of stations throughout the Asia-Pacific Region.
- **Objectives:**
  - Determine the status and trends in: concentrations of ambient air mercury species - Gaseous Oxidized Mercury (GOM), Particulate bound mercury (PBM2.5), Elemental mercury (GEM); and wet, dry and total atmospheric deposition of mercury.
  - Provide a robust dataset for regional and global model development and validation
  - Assist partner countries in developing their mercury monitoring and assessment capacity by providing training and best practices for multi-media sampling and analysis.
  - Exchange pilot network data and monitoring information among network partners.

5. Network Design Elements

- Science Advisory Group guides network decisions.
- Standard, network-wide procedures for field and laboratory operations, quality assurance, and data management adapted to Southeast/East Asia conditions.
- Single laboratory for sample analysis preferred; pilot network analysis performed by the mercury laboratory at the National Central University, Taiwan.
- Total mercury in rainwater; air concentrations of GEM, GOM, PBM2.5 at select locations.
- Sites in regionally representative areas; rural, urban, and suburban areas with estimated high levels of mercury emissions and deposition; and sensitive ecosystems.
- Three year operation of the pilot network, beginning September 2014; transition to fully operational network anticipated by 2017.
- New countries invited to join; network leverages existing monitoring, where possible. Figure 3. shows the current status of the network

6. APMMN Mercury Wet Deposition Sites

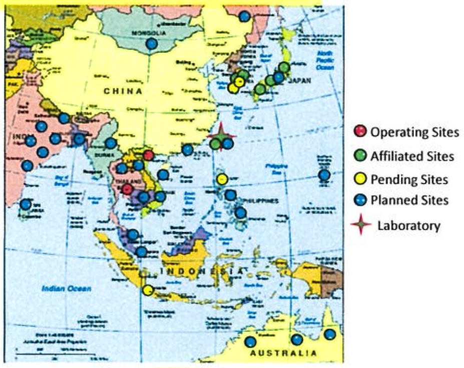


Figure 3. APMMN Site Status

7. Network Profile

- The Science Advisory Group developed and approved the Mercury Wet Deposition Network Field Standard Operating Procedures V.2.0. *APMMN* (2014). Figure 4. presents the samplers currently operating within the APMMN pilot. Eventually, one approved model will be used across the network.


NCON Model MDN 00-125-2 | NADP-style Aerochem 301 | Japanese-style Model A-TF1 | Taiwan-style MIC

Figure 4. Current APMMN Samplers

- Weekly samples are collected using automated wet only precipitation collection systems
- Sample bottles and glassware are changed every Tuesday
- Acid-cleaned glass funnels and 1L Teflon bottles are used for the Hg collections.
- National Central University, Taiwan quantifies Total Mercury by dual amalgamation cold vapor atomic fluorescence spectroscopy (CVAFS) after BrCl oxidation, $NH_2OH \bullet HCl$ neutralization, and $SnCl_2$ reduction (USEPA Method 1631, Revision E).

8. Future Capacity Building

- Develop new partnerships to expand regional monitoring coverage.
- Add data streams from affiliated national monitoring programs using either a comparison lab QA program or a single lab for all sites.
- Continue to provide training on methods of sampling and analysis of mercury in air and rainwater; expand to include other media (e.g, water, biota)
- Harmonize operation of continuous automated air mercury monitoring stations; expand regional measurements of air mercury species, including use of manual sampling and analysis methods.

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Characterization of wet and dry deposition of atmospheric mercury to a mountain background site in East Asia in 2009-2016

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Motivation and key findings

Wet and dry deposition of atmospheric Hg is the important atmospheric Hg pathway between air and terrestrial ecosystems. Although East Asia is the major atmospheric mercury (Hg) emission source region, studies about atmospheric Hg deposition in this region are still limited. In this study, we reported the wet and dry deposition of atmospheric Hg to the Lulin Atmospheric Background Station (LABS), a tropical mountain site in central Taiwan, from 2009 to 2016. Our results showed a clear seasonal cycle of Hg deposition flux. During 8 complete years, the annual wet flux was 27.3 μg.m^{-2}.yr^{-1}, about 3 times higher than wet fluxes at sites across eastern USA and the annual dry flux was 60.8 μg.m^{-2}.yr^{-1}, about 5 times the fluxes estimated at North American sites. This is the first long – term wet and dry deposition data reported in tropical mountain background in East Asia.

Site and methods

- Lulin Atmospheric Background Station (23.47°N, 120.87°E, 2862 m a.s.l.) was established in central Taiwan in 2006 to study the impact of regional and long-range transported air pollutants, including mercury (Hg).
- Concentrations of speciated atmospheric Hg, including gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM) and particulate Hg (PBM), were measured using the Tekran 2537/1130/1135 speciation unit. Dry deposition of speciated Hg was estimated using a bidirectional air-surface flux exchange model.
- Model setup: land use categories (LUC = mixed wood forest), leaf area index (LAI = 5), stomatal and soil emission potentials (Γ_{st} = 10; Γ_g =20).
- Weekly rainwater samples are manually collected every Tuesday. Concentrations of total mercury (THg) are determined using CVAFS (Tekran 2600).

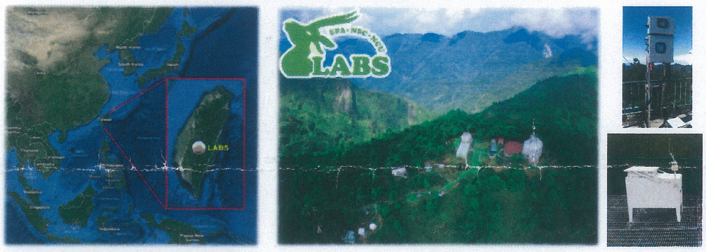


Figure 1. Lulin Atmospheric Background Station (LABS): location and scenery overview, and the instruments used in this study.

Results

1. Characteristic of Hg wet and dry deposition in 2009 - 2016

Table 1. Summary of GEM nighttime concentration, rain depth (precipitation), volume weighted mean concentration, dry and wet Hg deposition flux in 2009 – 2016.

	2009	2010	2011	2012	2013	2014	2015	2016
GEM nighttime (ng.m^{-3})	1.90	1.48	1.34	1.52	1.29	1.39	1.38	1.53
Rain depth(mm)	4991*	3171	3230	3521	3518	2539	2160	3207
Volume weighted mean (ng.L^{-1})	8.72*	9.62	7.71	13.08	6.96	6.62	5.04	6.53
Total wet deposition (μg.m^{-2})	43.52*	30.51	24.90	46.05	24.49	16.81	10.89	20.94
Total dry deposition (μg.m^{-2})	63.44*	68.38	57.06*	56.55*	51.79	57.00	61.70	70.15

*Note: 2009 precipitation data in August and September take from Alishan mountain sampling site
2009 total dry deposition (January to July); 2011 (Feb – Dec); 2012: (Jan – May and Sep – Dec)

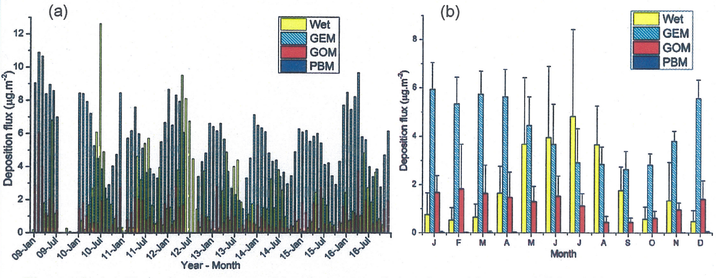


Figure 2. (a) Time series of monthly Hg wet and dry deposition, and (b) multi-year monthly average Hg wet and dry deposition at Mt. Lulin in 2009 – 2016 (error bar: +1sd).

Hg dry deposition is higher in spring and winter than the other season. GEM was the main contributor to the net Hg dry deposition. The wet deposition is concentrated from May to August, consistent with the raining season in Taiwan.

2. Atmospheric Hg diurnal and seasonal pattern

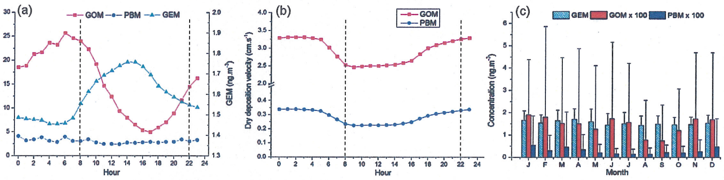


Figure 3. (a) Diurnal cycle of speciated Hg concentration, (b) dry deposition velocity of GOM and PBM and (c) monthly mean and standard deviation of Hg species at LABS in 2009 - 2016.

3. Hg dry deposition day and night

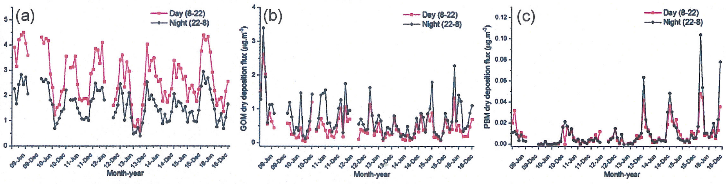


Figure 4. Time series of daytime (8 – 22) and nighttime (22 – 8) monthly Hg dry deposition flux in 2009 - 2016 for (a) GEM, (b) GOM and (c) PBM.

4. Sensitivity test the uncertainty of GEM dry deposition flux

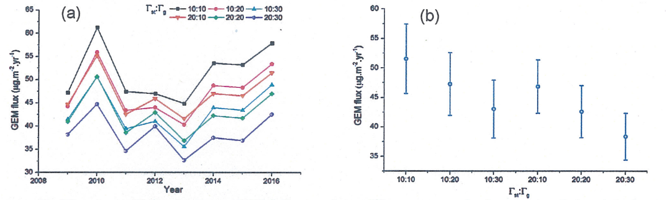


Figure 5. The sensitivity test on GEM flux using difference emission potentials. (a) Annual variations of GEM dry deposition flux and (b) Multi-year mean GEM dry deposition flux.

The multi-year GEM mean dry deposition flux ranged from 51.5 – 38.4 μg.m^{-2}.yr^{-1} from using the highest and lowest emission potentials, demonstrating the reliability of the GEM dry deposition flux estimated in this study.

5. Wet Hg deposition correlation and implication

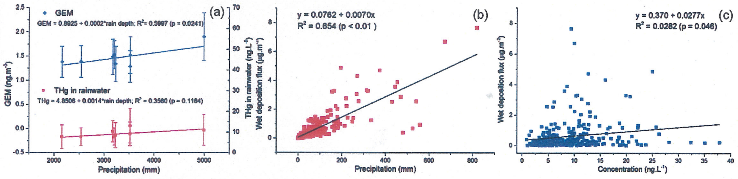


Figure 6. Correlation plot of annual mean GEM nighttime concentration and THg vs precipitation (a), relationship between weekly precipitation and Hg concentration vs wet Hg deposition flux (b and c).

Weekly wet deposition fluxes and rainfall were highly correlated. The moderate correlation of GEM and total Hg in rainwater samples (THg) with precipitation indicated the signature of the large scale meteorology influence.

6. Comparison with other studies

Table 2. Comparison of wet and dry Hg deposition with other studies

Location	Dry deposition	Wet deposition	Reference
Mt. Lulin (Taiwan)	60.8	27.3	(This study)
Kejimkujik National Park	34.4	7.1	Zhang et al. 2012
10 sites around Japan	8.0 (4.4 – 13.2)	12.8 (5.8 – 17.7)	Sakata et al. 2005
Europe	4.0 – 32.5	7 - 36	X. W. Fu (review 2015)
15 location in Eastern USA	12.3 (3.5 – 23.4)	9.6 (4.4 – 19.7)	Martin R. Risch 2012
Mt.Gongga (China)	35.5	21.6	Fu et.al, 2010
Mt.Ailao Yunan (China)	68.2	7.2	X.W.Fu et.al, 2016
19 sites in North America	4.6 – 23.8	(9.4) 5.4 – 21	Zhang et al. 2016
Mauna Loa (US)	56.5	-	Zhang et al. 2016

Summary

- Wet and dry mercury deposition flux at Mt. Lulin are significantly higher than those at the sites in Japan and North America.
- The annual pattern of Hg wet deposition was opposite with that Hg dry deposition. The wet deposition contributed about 30% of total Hg deposition.
- Nighttime GOM dry deposition (8.09 ± 1.96 μg.m^{-2}.yr^{-1}) was higher than that of daytime (5.21 ± 1.58 μg.m^{-2}.yr^{-1}) due to higher GOM concentration and wind speed at night. Sensitivity test indicated that the GEM deposition flux in this study is in reasonable range. With varying soil and stomatal emission potentials, GEM was always the main contributor to the net dry Hg deposition.
- Large scale meteorology can influence wet and dry Hg deposition budget at Mt. Lulin.

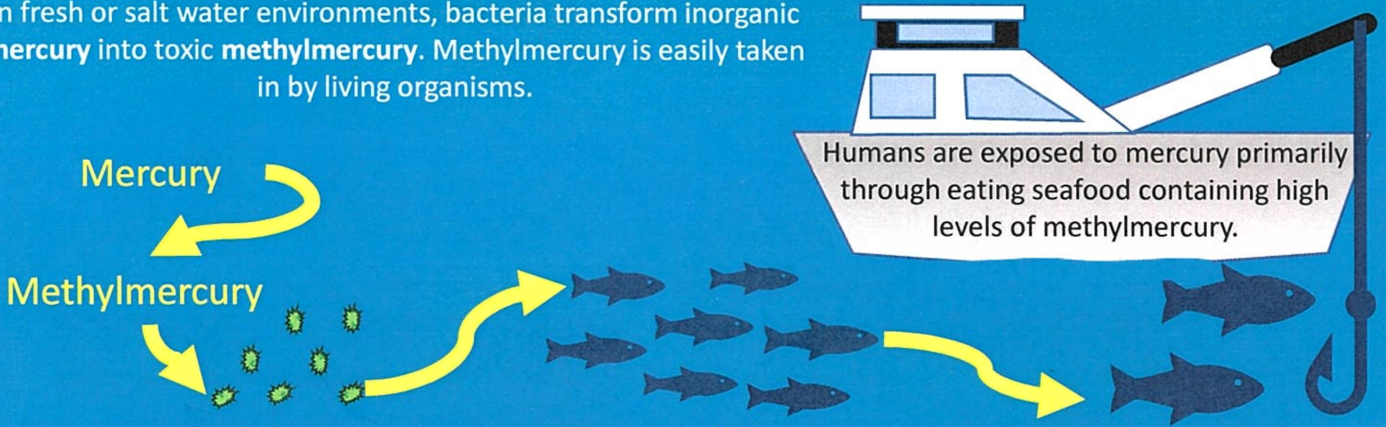
Acknowledgment:
This study is financially supported by the Environmental Protection Administration and Ministry of Science and Technology, Taiwan.

Dartmouth Toxic Metals
Superfund Research Program

80
Hg

Mercury: From Source to Seafood

How does mercury get into seafood?



In fresh or salt water environments, bacteria transform inorganic **mercury** into toxic **methylmercury**. Methylmercury is easily taken in by living organisms.

Humans are exposed to mercury primarily through eating seafood containing high levels of methylmercury.

Mercury

Methylmercury

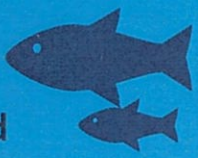
Plankton
10,000 times more methylmercury than in water

Prey Fish
1-10,000,000 times more methylmercury than in water

Predatory Fish
10-100,000,000 times more methylmercury than in water

In a process called **biomagnification**, methylmercury becomes more concentrated as it moves up the aquatic food chain.

What are the risks and benefits of eating seafood?



Health Risks from Mercury

Mercury crosses the blood-brain barrier, causing :

- Problems with memory, speech, fine motor skills, personality development and cognitive function;
- Neurological problems during development in young children;
- Heart and immune health problems with high mercury exposure.

Health Benefits of Seafood

Seafood provides:

- Nutrients essential for healthy growth and development in young children;
- The highest levels of omega-3 polyunsaturated fatty acids of any foods, which improve heart health, liver function and eyesight;
- Essential trace elements and vitamins like selenium, iodine and vitamin D.

How can I enjoy the benefits of seafood and limit risks of methylmercury exposure?

Be an informed seafood consumer and know the sources of your food.

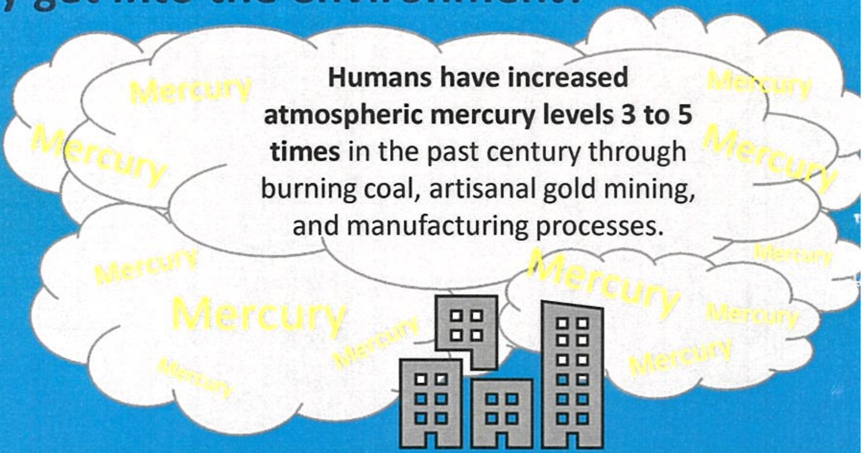
Limit your consumption of predatory fish like shark, swordfish and tuna.

Eat seafood lower on the food chain like crabs, clams, salmon and sardines.

Reducing mercury for a healthier world

How does mercury get into the environment?

Mercury in rocks and soils is naturally released into the atmosphere through volcanic eruptions and forest fires.



Humans have increased atmospheric mercury levels 3 to 5 times in the past century through burning coal, artisanal gold mining, and manufacturing processes.

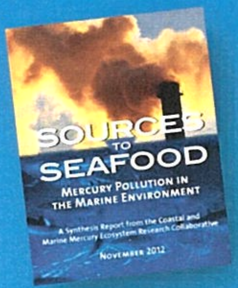
Mercury from the atmosphere settles in aquatic systems through rainwater and snowfall, and mercury released from point sources like chemical plants leaks into local estuaries and other nearby bodies of water.

How is Dartmouth Superfund research addressing mercury?

We want to understand the environmental components that influence methylmercury production and biomagnification in different aquatic systems. Our current research focuses on two mercury-contaminated sites: the Penobscot River in Maine and Berry's Creek in New Jersey. By looking at how environmental factors like salinity and water temperature affect both the conversion of mercury to toxic methylmercury and its bioaccumulation in the aquatic food chain, we are learning what drives these processes, informing how to reduce human exposure and improve coastal ecosystem health.

We work with New Hampshire and Vermont high school science classes on an annual project collecting dragonfly larvae as a measure of mercury levels in local ecosystems. The results are added to a national mercury monitoring database, and our partnership advances mercury research and inspires the next generation of environmental scientists.

How is our research connecting mercury science and policy?

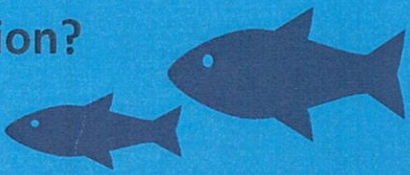


SOURCES TO SEAFOOD
MERCURY POLLUTION IN THE MARINE ENVIRONMENT
A Synthesis Report from the Coastal and Marine Mercury Ecosystem Research Collaborative
NOVEMBER 2012

The Coastal and Marine Mercury Ecosystem Research Collaborative (C-MERC) papers focus on the sources, cycling, and bioaccumulation of mercury to help policymakers and the public understand mercury's effects on marine ecosystems and people: www.c-merc.org

Our C-MERC science helped inform the Minamata Convention, a global commitment to reducing mercury in the environment and discharges to water. As of May 2017, the agreement is ratified by over 50 countries, allowing it to enter into full force in August 2017. Learn more at: http://mercuryconvention.org

Where can I find more information?



Watch our video **Mercury: From Source to Seafood**: www.source2seafood.org

Visit our program website: www.dartmouth.edu/~toxmetal

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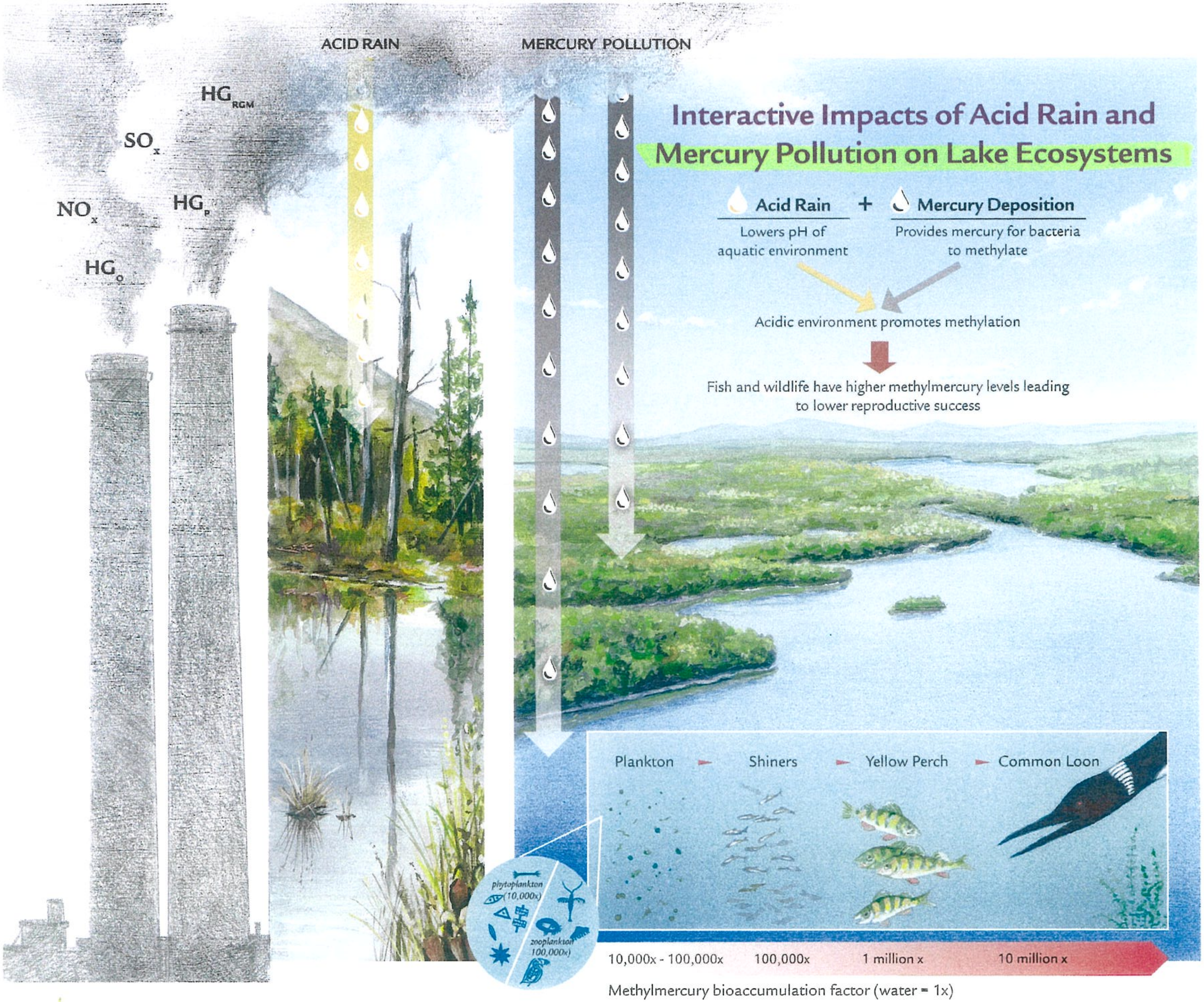
NIH National Institute of Environmental Health Sciences
Superfund Research Program

This project is supported by NIH Grant number P42ES007373 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of Environmental Health Sciences, or the National Institutes of Health.



Interactive Impacts of Acid Rain and Mercury Pollution on Lake Ecosystems

Acid Rain + **Mercury Deposition**

Lowers pH of aquatic environment

Provides mercury for bacteria to methylate

Acidic environment promotes methylation

Fish and wildlife have higher methylmercury levels leading to lower reproductive success

Methylmercury bioaccumulation factor (water = 1x)

Species at Risk


River Otter


Bald Eagle


Northern Long-eared Bat


Rusty Blackbird


Yellow Perch

ICMGP2017

Linking Science and Policy to Support the Implementation of the Minamata Convention

13th International Conference on Mercury as a Global Pollutant

Providence, Rhode Island | July 16–21, 2017

Linking Science and Policy to Support the Implementation of the Minamata Convention

Henrik Selin, Susan Keane, Noelle Eckley Selin, Shuxiao Wang, Dominique Bally and Kenneth Davis

SYTHESIS PAPER FOR GROUP 4 FOR THE 2017 INTERNATIONAL CONFERENCE ON MERCURY AS A GLOBAL POLLUTANT, PROVIDENCE, RHODE ISLAND, USA, JULY 16-21, 2017

DRAFT – PLEASE DO NOT CITE OR QUOTE
JUNE 28, 2017

Comments most welcome! Please e-mail all comments to Henrik Selin (selin@bu.edu) and Susan Keane (skeane@nrdc.org)

Abstract

The Minamata Convention on Mercury, which sets out the objective to "protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds" (Article 1), entered into force in 2017. As the convention, which outlines a life-cycle approach to the production, use, emissions, releases and handling of mercury, moves into the implementation phase, different types of scientific information and assessments are critically needed to support decision-making and management. This article identifies and discusses ways in which the scientific community can help mobilize knowledge in support of mercury abatement and the realization of the convention's objective. It specifically offers guidance for researchers, policy makers, and stakeholders who wish to connect with international, national, and local efforts related to three focal areas: i) uses, emissions and releases; ii) impacts and effectiveness; and iii) awareness raising and science-based education. The article ends with a discussion of the future of mercury science and governance.

Introduction

The Minamata Convention on Mercury, which aims to "protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds" (Article 1), was adopted in 2013 (Andresen et al. 2013, Eriksen and Perrez 2014, Selin 2014a).[1] The world's countries, with the participation of many intergovernmental- and nongovernmental organizations, negotiated the Convention to outline a set of shared principles, standards and rules. Countries voluntarily decide whether to become a party to an international environmental agreement like the

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[1] The authors thank David Evers and Lesley Sloss for helpful comments on earlier drafts of this article as well as David Streets and Hannah Horowitz for discussions about and supplementary data on emissions, releases, and products. We thank the Massachusetts Institute of Technology International Policy Laboratory for financial support.

Minamata Convention, but once they commit to do so its provisions bind parties.[2] The widespread support for the Minamata Convention is reflected in its entry into force in August, 2017, 90 days after the fiftieth country ratified it. The number of parties is expected to increase over the next decade.[3]

The Convention builds upon an extensive body of scientific knowledge on mercury as well as on decades of domestic and international policy efforts to manage its environmental hazards. Science played a key role in establishing recognition for mercury as a global pollutant (United Nations Environment Programme 2002, 2008). Scientific knowledge helps to understand mercury's global distribution (Synthesis paper 1), its changing cycling in response to local perturbations (Synthesis paper 2), and its health and environmental impacts (Synthesis paper 3). Voluntary efforts under the United Nations Environment Programme (UN Environment) Global Mercury Partnership to reduce mercury use and emissions and to draw attention to environmental and human health risks from mercury date back to the early 2000s (Selin and Selin 2006).[4] The Convention, a legally-binding agreement, builds on these efforts as it outlines a life-cycle approach to the production, use, emissions, releases and handling of mercury and mercury compounds.

As the Convention moves into its implementation phase, different types of scientific information and assessments can support decision-making. The relationship between science and environmental treaty implementation is complex, as there is not a direct, causal link between more scientific data and "better" policy-making and outcomes (Shackley and Wynne 1995). Rather, the interplay between science and policy is multifaceted and often case-specific. Yet, studies show that the implementation of environmental treaties can benefit from information and assessments that are scientifically credible, policy relevant and politically salient (Farrell et al. 2001, Selin and Eckley 2003, Mitchell 2006). In addition, the field of sustainability science analyzes how societies can guide or manage interrelated human and environment systems in support of a sustainability transition (Clark and Dickson 2003, Kates 2011).

This article identifies and discusses some major ways in which the scientific community, across a large number of disciplines and fields, can help mobilize knowledge in support of the implementation of the Convention and the realization of its ultimate objective. It specifically examines three Convention focal areas where research in the natural sciences, engineering, and social sciences can support mercury management and policy-making: i) uses, emissions and releases; ii) impacts and effectiveness; and iii) awareness raising and science-based education. For each of these areas, we synthesize the status of scientific knowledge, identify research needs, and offer guidance for researchers, policy

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[2] The same is true for the European Union, which joined separately of its member states as a Regional Economic Integration Organization (Selin and VanDeveer 2015).

[3] For an updated list of parties, see the Minamata Convention website: http://www.mercuryconvention.org/

[4] For more on the Global Mercury Partnership and its different work areas, see: http://www.unep.org/chemicalsandwaste/global-mercury-partnership

makers, and stakeholders who wish to connect with international, national, and local efforts related to the Convention.

The next section provides a brief summary of the structure and content of the Convention. This is followed by a discussion of how scientific work can support convention-related activities in the three major areas. The article ends with a discussion of the future of mercury science and governance.

Minamata Convention Approaches to Mercury Management

Mercury is a chemical element that is intentionally used in many products and industrial processes and also emitted and released into the environment as a byproduct of a multitude of human activities. Designing a convention with a comprehensive life-cycle focus covering all these areas was a challenging task. Negotiators also needed to accommodate different national interests and find ways to assist developing countries with domestic implementation. Table 1 summarizes key dates in the development and implementation of the Convention. All parts of the treaty are legally binding for the parties, but some treaty provisions express required actions (using the word "shall") while some are hortatory (using words such as "should" or "may"). The core of the Convention is the "control" provisions and "enabling" provisions, described below. Other Convention articles cover introductory material, definitions, and administrative matters.

Control Provisions

The control provisions (Articles 3-12) identify actions that parties must take to address mercury supply, trade, use, management, emissions and releases to the environment. They apply to cases where mercury is intentionally extracted and used in a commercial product or industrial process, as well as where mercury is present in a raw material and emitted and released during processing or combustion. Provisions that restrict primary mercury mining and the use of excess mercury from decommissioned chlor-alkali facilities aim to reduce the supply of mercury. International trade in allowed uses of mercury is controlled through a system of prior informed consent (e.g. the national government of an importing country must explicitly approve the import of mercury before it can be exported from a supplier in another country).

Intentional mercury use is controlled through requirements to phase out its use in a large number of mercury-added products and industrial processes where mercury is used. The Convention establishes phase-out dates for specified products and processes (see Table 1), but parties may apply for exemptions that allow extensions of up to 10 years. Mercury use in artisanal and small-scale gold mining (ASGM) is treated distinctly from other mercury uses due to its frequently informal nature, widespread occurrence, and close connections with rural poverty and human development. ASGM is the largest global source of mercury use and release into the environment (United Nations Environment Programme 2013b) as well as the most common sector where humans are exposed directly to inorganic mercury.

Table 1: Main Convention Dates, Requirements and Deadlines

UN Environment Governing Council agrees to begin negotiations on a legally binding agreement on mercury	2009
Minamata Convention adopted and opened for signature	2013
Entry into force of the Minamata Convention	2017
First Conference of Parties	2017
Prohibition of new mercury mining	Upon entry into force for a Party
Phase-out of mercury use in acetaldehyde production[5,6]	2018
Deadline to reduce mercury use in VCM production by 50% (2010 baseline)	2020
Phase-out of mercury use in mercury-added products listed in Annex A[4]	2020
Deadline for submitting ASGM National Action Plans to the Secretariat	3 years after entry into force for Party (e.g. earliest 2020), or 3 years after notifying the Secretariat that ASGM activity is more than insignificant, whichever is later
Deadline for Parties to require use of BAT and BEP for new sources from emissions categories listed in Annex D	5 years after entry into force for a Party (e.g. earliest 2022)
Deadline to complete first effectiveness evaluation	2023
Phase-out of mercury use in chlor-alkali production[4]	2025
Deadline for Parties to require use of ELV, BAT, BEP or alternative measures for existing sources from emissions categories listed in Annex D	10 years after entry into force for a Party (e.g. earliest 2027)
Phase-out of existing primary mercury mining	15 years after entry into force for a party (e.g. earliest 2032)

Pollution controls from the use and processing of materials that contain mercury impurities are divided into emissions to air and releases to land and water. Parties must control atmospheric mercury emissions from certain sectors by applying best available techniques (BAT) and best environmental practices (BEP) to new sources. A combination of other approaches can be used for existing sources, including a multi-pollutant control strategy that would deliver co-benefits in the control of mercury emissions while aiming to control other pollutants. Controls on releases to water and land are incorporated into obligations for products, industrial processes, and sources of atmospheric emissions, but parties must also control releases from other relevant sources. Parties must manage mercury and mercury containing waste in an environmentally sound manner, taking into account the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal.

Enabling Provisions

The enabling provisions (Articles 13-24) are intended to help the parties implement and further develop the Convention, and to track progress and measure effectiveness of

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[5] Mercury use in acetaldehyde production is not known to be taking place currently.

[6] Parties may apply for exemptions pushing back phase-out dates up to 10 years.

related management and policy measures. The Convention establishes an administrative Secretariat and the Conference of the Parties (COP), the main decision-making body on issues related to treaty implementation and development. The Convention also established a facilitative implementation and compliance committee to promote implementation, review compliance, and explore ways to assist parties that have difficulty fulfilling their obligations. Critically, the Convention defines a new mechanism for the provision of adequate, predictable and timely financial resources to developing countries that includes the Global Environment Facility Trust Fund, which should operate alongside other funding sources.

Enabling provisions call on parties to promote strategies and programs for protecting public health and the environment from mercury pollution, share information with each other, and inform the public about mercury pollution and its impacts. The Convention also includes language that encourages parties to develop inventories of mercury use and release and technologies to reduce them, conduct modeling and monitoring of mercury in the environment, and identify impacts of mercury on human health and the environment. To help track progress, parties are required to report through the Secretariat on measures that they have taken toward implementation and their effectiveness and possible challenges in meeting Convention objectives. Enabling provisions also call on all the parties to cooperate to provide technical and capacity building assistance to developing countries.

The next three sections examine how the work of the scientific community can contribute to treaty implementation in three main issue areas. Table 2 illustrates the relationship of these three areas with the main relevant convention articles. While the first area comprises control provisions, the latter two relate to the enabling provisions. Each section first synthesizes the existing status of key scientific understandings and then identifies major knowledge gaps and future research needs.

Table 2: Three Key Convention Areas and Related Articles

Convention Area	**Minamata Convention Articles**
Uses, emissions and releases	Article 3 – Supply and trade Article 4 – Mercury-added products Article 5 – Process that use mercury Article 6 – Exemption to phase-out dates Article 7 – ASGM Article 8 – Emissions Article 9 – Releases Article 10 – Storage Article 11 – Waste Article 12 – Contaminated Sites
Impacts and effectiveness	Article 15 – Implementation and compliance Article 19 – Research, development, monitoring Article 21 – Reporting Article 22 – Effectiveness evaluation
Awareness raising and science-based education	Article 13 – Financial mechanism Article 14 – Capacity building, technical assistance and technology transfer

	Article 16 – Health aspects Article 17 – Information exchange Article 18 – Information, awareness, education

Uses, Emissions and Releases

The control provisions address both intentional uses of mercury and releases of byproduct mercury (Table 2). Article 3 covers the phase-out of mercury supply, including from primary mining, and trade restrictions for exporting and importing mercury. Article 4 prohibits the manufacture, import or export of many mercury-added products, including batteries, switches, relays, lamps, pesticides, and cosmetics. The use of dental fillings containing mercury amalgam should to be discontinued, although no deadline is set. Article 5 obliges the parties to phase out mercury use in two manufacturing processes (chlor-alkali production and acetaldehyde production) and to restrict mercury use in three others (vinyl chloride monomer production (VCM), sodium or potassium methylate or ethylate production, and the production of polyurethane). Article 6 allows parties to apply for time-limited extensions to set phase out dates. Article 7 obligates parties to take steps to reduce and eliminate mercury use in ASGM.

Articles 8 and 9 address mercury emissions to air and releases to land and water. Parties are required to establish and maintain an inventory of emissions and releases from relevant sources. The initial list of sources of air emissions includes coal-fired power plants, coal-fired industrial boilers, non-ferrous metals (smelting and roasting), waste incineration, and cement clinker production. For mercury releases, parties are required to identify relevant sources. Each party shall take measures to control and, where feasible, reduce mercury emissions and releases. The use of BAT and BEP is required for new sources. A party may apply the same measures to existing sources or may adopt different measures including emission limit values (ELVs). Articles 10 and 11 cover mercury storage requirements and environmentally sound waste management practices. Article 12 encourages parties to develop strategies for identifying and assessing mercury-contaminated sites.

Existing Knowledge

Figure 1 synthesizes available information on global-scale budgets of mercury, organized by Convention article for the categories of uses, emissions, and releases.

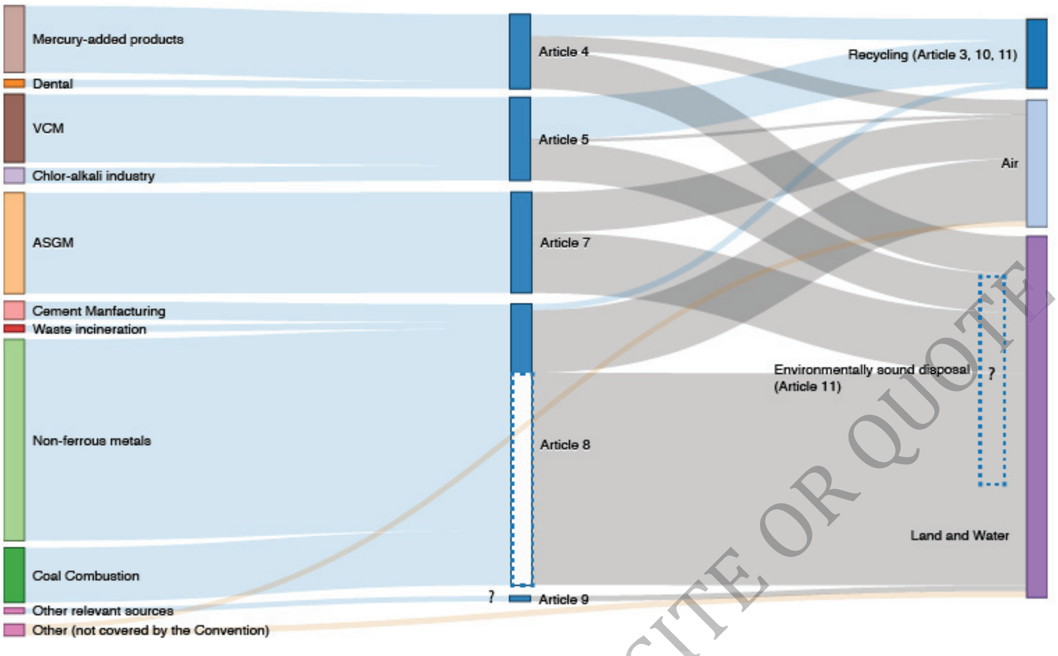

Figure 1. Global mercury budget for uses, emissions, and releases. Data from (Horowitz et al. 2014, Streets et al. 2017, United Nations Environment Programme 2017c). Question marks and dotted box indicate non-quantitative estimates. Dark blue represents Convention articles.

Related to Article 3 on mercury supply, Streets et al. (2017) estimates that primary mining accounts for 27 percent of all-time cumulative releases to the environment. The commercial use of mercury derived from such mining and its re-use in products (Article 4) and processes (Article 5) has produced a large anthropogenic source of mercury in the global environment (Horowitz et al. 2014). For Figure 1, inputs into Article 4 (1200 Mg, with an uncertainty range of 860-1540 Mg) are specified from UN Environment (2017) as the sum of mercury consumption from batteries, measuring and control devices, lamps, electrical and electronic devices, and mercury compounds and other applications. It is estimated that 20% of Article 4 Hg consumption is released to air, 51% to land and water, and 29% recycled (Horowitz et al., 2014 and personal communication). For Article 5 processes, Figure 1 estimates inputs from the VCM industry (1230 Mg, uncertainty range 1210-1240 Mg) and the chlor-alkali industry (280 Mg, uncertainty range 230-320 Mg) (United Nations Environment Programme 2017c). Emissions, release, and recycling fractions for Article 5 are estimated as 4%, 46%, and 50% respectively (Horowitz et al., 2014 and personal communication).

In implementing Convention-mandated phase-outs and restrictions of intentional uses in products and processes, countries can draw on extensive technical knowledge on substitutes and alternate reduction measures, including from collaborative initiatives that were carried out under the Global Mercury Partnership. For most commercial products, mercury-free alternatives already exist that can be readily substituted for older ones that still contain mercury. The same is true for the main industrial processes that traditionally used mercury. Here, much focus is on phasing out the use of mercury catalysts in the

VCM industry, which is the largest use of mercury in China. Some policy recommendations suggest enhanced reporting and establishment of closed-loop systems (Wang et al. 2016). However, the ultimate solution for this sector, similar to other industrial processes that used to use mercury, is to develop a mercury-free catalyst and completely eliminate the need for mercury in the VCM industry.

Several studies quantify mercury emissions to air (Kim et al. 2010, Pacyna et al. 2010, Pirrone et al. 2010, United Nations Environment Programme 2013b, Zhang et al. 2015). Figure 1 differentiates emissions by Convention article, following Streets et al. (2017) . For Article 8 sources (coal-fired power plants, coal-fired industrial boilers, non-ferrous metals, waste incineration, and cement production), emissions to air are estimated as 1130 Mg, including totals from all relevant sectors but excluding the residential and transportation coal use not covered by the Convention. A small amount of mercury (110 Mg) from non-ferrous metal consumption is estimated to be recycled (D. Streets, personal communication). For Article 7, the estimate is 730 Mg from ASGM. Emission inventories are thought to be relatively accurate for some sources such as energy and industrial sectors, but with large uncertainties for other sources such as ASGM (Pacyna et al. 2016); the uncertainty range for ASGM is 410-1040 Mg (United Nations Environment Programme 2013b). Emissions to air from sources not covered by the Convention (97 Mg) include coal from residential use and transportation (34.5 Mg, Streets, personal communication), iron and steel, and oil combustion sources.

Some studies explore the various mercury emission control options for major stationary sources (including coal-fired power plants) and their degrees of effectiveness (Krishnakumar et al. 2012, Sloss 2012, Trovant 2013, Ancora et al. 2016, Hu and Cheng 2016). Importantly, parties may formulate their own national BAT and BEP standards (as well as ELV-equivalents) for mercury emissions from different stationary sources based on a combination of domestic technical and socio-economic factors (Lin et al. 2017). As these emission standards may vary across different regions and countries, there is a general expectation that they should be strengthened over time. Countries may also apply different metrics when formulating their emission standards. For example, the United States currently uses performance metrics (lb/Btu) while others such as China and the European Union apply concentration limits ($\mu g/m^3$).

A few more recent studies quantify mercury releases to land and water (United Nations Environment Programme 2013b, Liu et al. 2016, Kocman et al. 2017). One study estimates that cumulative, all-time total mercury releases to land and water are 2.3 times emissions to air (Streets et al. 2017). Some case studies address integrated mercury flows in several countries (Chakraborty et al. 2013, Hui et al. 2016). Article 9 of the Convention addresses releases to land and water from "relevant point sources not addressed in other provisions" of the Convention. Each party is to identify any such sources no later than three years after the date of entry into force for it; these to date unidentified sources are illustrated as a non-quantified source in Figure 1. Releases to land and water from sources addressed in other provisions of the Convention (Articles 4, 5, 7, and 8) are quantified in Figure 1 following Streets et al. (2017). In particular, releases from Article 8 are large, but specific provisions of the Convention in Article 8 are limited to guidance addressing "the need to minimize cross-media effects." This is indicated by the dashed component of the Article 8 box in Figure 1.

As countries phase out intentional mercury uses, there is a need to deal with mercury wastes in the form of discarded goods that contain mercury The COP will set threshold values for mercury content for the classification of mercury waste. Here, the COP may build on Basel Convention Technical Guidelines for the storage and disposal of mercury wastes. Also, the capture of by-product mercury from mining and the increasing use of mercury free processes and products will result in the accumulation of solid excess mercury. Regional assessments of projected excess mercury creating storage and disposal challenges have been completed for Asia, Europe, Central America and the Latin America/Caribbean regions. Excess supply accumulated between 2010 and 2050 across these regions may exceed 28,000-46,000 tons (Maxson 2009, United Nations Environment Programme 2014, European Union 2015). The quantities of releases to land and water that are diverted to environmentally-sound disposal (Article 11) are unknown (indicated by the dashed box in Figure 1), although this is the desired outcome for waste mercury.

Global mercury emission inventories of anthropogenic sources typically omit contributions of sites contaminated with high mercury levels relative to local background from historical accumulation. Such contamination is the result of different activities, including mercury mining and smelting, ASGM, large scale precious metal processing, non-ferrous metal production, and major industrial uses in the chlor-alkali industry and other sectors. One study estimates that over 3000 mercury-contaminated sites release about 137-260 metric tons of mercury annually to the atmosphere and the hydrosphere (Kocman et al. 2013). Even if contaminated sites based on existing data only make up a small percentage of total atmospheric emissions, they are important sources, especially for local water pollution where many sites are located in coastal areas impacting rivers, estuaries, and oceans (Randall and Chattopadhyay 2013).

Areas For Further Work

Many countries need to establish an inventory of mercury use, emissions and releases. The UN Environment Mercury Inventory Toolkit was developed for this purpose. There is a lack of localized emission factors that reflect the situation of different countries, especially for developing countries due to the high cost of sampling and analytical methods. To improve mercury inventories, several measurement studies are needed. These include: the development of cost-effective sampling and analytical methods; measurements of mercury behavior across newly employed air pollution control devices; continuous measurements of mercury transformation and speciation under different operational conditions and mercury emission from sources with large fluctuations (e.g., waste incinerators, crematories); measurements of emission factors for mercury releases; and measurements of mercury emission factors of contaminated sites.

Most studies do not account for mercury demand using a supply chain perspective, which can provide more information on the drivers of emissions and help identify activities that are interconnected through waste/byproduct flows (Hui et al. 2016, Wu et al. 2016). Developing a robust, detailed, bottom-up inventory that includes all relevant sources requires establishing a comprehensive national system for mercury material flows to track the mercury supply and trade in the society and movement in both air, water and soil. In many countries, especially developing ones, this is challenging. However, further studies in this area can help guide policy decisions to identify critical mercury emission/release sources and avoid secondary atmospheric mercury emissions. Researchers can also help develop manufacturing processes that reduce or eliminate mercury uses as well as new mercury-free products.

Scientists can assist with the development and deployment of technologies to control mercury emissions and releases, determining ELVs as well as designing national plans and expected outcomes. It will be important to understand the cost-effectiveness of various mercury control measures, which is challenging due to the limited information on cost of mercury control measures, and difficulties in predicting cost trends and technical innovations. However, costs of mercury control measures could decrease due to economies of scale, commercial maturity, or technical innovation. Also, because different air pollution control devices result in different speciation profiles for the emitted (and captured) mercury, the choice of specific devices influences not only the absolute amount of mercury emitted, but also its transport and spatial deposition, which in turn determines who will experience the benefits of policy actions (Giang et al. 2015).

For releases of mercury to water and land, engineers and scientists may help identify the most critical sources to control as well as develop the control measures and standards. For air emissions, a group of technical experts brought together by UN Environment has drafted guidance on BAT and BEP to assist parties in fulfilling their obligations (United Nations Environment Programme 2015). Where ELVs are used in place of BAT, they must reflect levels that can be achieved with BAT. Therefore, policy-makers will need to rely on scientists to establish and regularly review ELVs to take account of progress of BATs and ensure that ELVs are consistence with this progress. As also discussed further below, scientists can also play important roles in finding better ways to reduce both atmospheric emissions and releases to water and land from ASGM-related activities.

Although the control measures under each Article are quite different, they are environmentally linked. Measures to comply with one Article may lead to the increase of mercury addressed by another Article. For example, measures to curb mercury emissions can result in the capturing and storage of more mercury in the form of solid waste such as fly ash or gypsum from flue gas desulfurization. Once these solid wastes are utilized in a high temperature process (such as cement clinker), mercury may be emitted to the air (Wang et al. 2014). As such, policy decisions should consider the life cycle of mercury (Lin et al. 2017). In support, research is needed to measure mercury emissions and releases from major sources and establish national inventories, track mercury material flows, and monitor how emissions and releases change over time.

To address the large uncertainties in global scale contributions of mercury emissions to the atmosphere and releases to aquatic environments from contaminated sites, there is a need for further systematic and harmonized measurements and data collection, model refinements, and analysis (Kocman et al. 2013). While North America and Europe struggle to address older contaminated sites, the number and severity of mercury-contaminated sites continue to increase especially in Asia but also in other parts of the world (Li et al. 2009, Kocman et al. 2013). Expanding knowledge and means for environmentally safe handling of mercury wastes as well as further development and dissemination of guidelines and methods for easier and more cost effective remediation practices for contaminated sites remain important issues (Wang et al. 2012, Randall and Chattopadhyay 2013, Xu et al. 2015).

Because countries face significant problems with mercury-contaminated sites, remediation issues are of a worldwide concern. The most frequently used remediation method is soil excavation and disposal (Wang et al. 2012). Such an approach, however, is often both expensive and rudimentary, and it also only makes sense when the mercury in soil is localized rather then dispersed, which is often the case. As a result, there are increased efforts to develop alternative methods and techniques for better and cheaper remediation (Wang et al. 2012, Randall and Chattopadhyay 2013, Xu et al. 2015). Here, engineers and scientists can play important roles to further develop and test different in-situ and ex-situ options. Importantly, the choice of specific remedial approach should be focused on site-specific parameters, as local conditions can vary tremendously across different sites (Randall and Chattopadhyay 2013, Xu et al. 2015).

Impacts and Effectiveness

Several Convention articles relate to efforts to evaluate its effectiveness toward meeting its goal of protecting the environment and human health from mercury. Some of these articles focus on generating implementation data and making such data available through public reporting. This includes Article 21, which mandates that parties report on national measures and their effectiveness to the Secretariat; Article 15, which creates an implementation and compliance committee to review implementation progress and help parties that face challenges; Article 19, which mandates that parties develop and improve methods for both modeling and monitoring of mercury in vulnerable human populations and in targeted environmental media; and Article 22,which requires the COP to carry out periodic effectiveness evaluations, the first of which must begin no later than six years after the Convention enters into force (2023 at the latest).

Overall, the purpose of effectiveness evaluation is to determine whether the Convention is meeting its stated goal. To this end, the effectiveness evaluation ultimately needs to assess the link between implementation measures and changes in mercury levels in the environment, and subsequently changes in human and environmental exposures and impacts. Because carrying out this complicated multi-chain analysis is a substantial scientific challenge, it is likely that the effectiveness evaluations, at least initially, will focus on mainly process-related aspects of implementing the Convention, as well as policy outcomes that can be observed in the short-term. Accordingly, Article 22 requires the consideration of scientific, environmental, technical, financial and economic factors in the evaluation of Convention effectiveness.

Existing Knowledge

Identifying whether the Convention is protecting human health and the environment from mercury involves mobilizing scientific knowledge across a complex chain of causality and attribution. Changes in anthropogenic mercury emissions may result from implementation of Convention provisions; from other socio-economic or environmental policies; or from both influences concurrently. Changes in emissions in turn result in changes in mercury deposition to ecosystems, and subsequent conversion to methylmercury. Finally, changes in human and environmental exposure and adverse impacts result from mercury exposure. Several areas of scientific research and data collection, highlighted in this section, provide methods and information integral to connecting these elements into a causal chain for impact assessment.

Much scientific research to date has aimed to reduce uncertainties in factors that affect the first part of this causal chain, namely mercury emissions, cycling and environmental behavior. In addition to these uncertainties, which reflect incomplete scientific understanding, some factors are also highly variable and source- and location-dependent. For example, the processes that drive rates of atmospheric depletion and deposition, such as mercury oxidation (Ariya et al. 2015) and meteorological factors, vary over spatial and temporal scales. Once mercury is deposited on land or over water bodies, local conditions (such as temperature and the amounts of oxygen, organic matter, and sulfate) drive the transformation of elemental mercury into more toxic methylmercury (Faganeli et al. 2014, Wentz et al. 2014, Gascon Diez et al. 2016). Both mercury exposure (e.g. through varying levels of fish consumption) and health outcomes (e.g. through differences in susceptibility to mercury impacts) vary among populations and can change over time due to factors not related to mercury policy. Thus, efforts to identify policy signals must account for factors other than the Convention that might impact outcomes when designing sampling strategies.

Measuring and monitoring of levels and trends of mercury in the environment is another key input to the policy-to-impacts causal chain. Monitoring provides direct observations on mercury in the environment and can identify significantly impacted ecosystems and human populations, and forms a basis for testing and calibrating models. For example, monitoring near specific emission sources has been able to detect changes in mercury deposition over relatively short time scales (e.g. Lindberg et al. 2007). Local- to regional-scale observations can be critical not only for assessing compliance with Convention measures, but also for demonstrating progress on relatively short time scales that can be reasonably attributed to source reductions. In contrast, the response of global atmospheric mercury concentrations to Convention measures will be complex and influenced by a wide range of environmental and policy factors. In fact, global deposition may still actually increase in the short-term even under some emissions reduction scenarios, as re-emission of legacy mercury exceeds sequestration in the environment (Sunderland and Selin 2013).

Some work attempts to relate environmental mercury trends to global changes in mercury emissions due to various policy actions. Atmospheric mercury monitored over the past few decades show mixed trends. Both decreasing (Zhang et al. 2016) and more recently increasing (Martin et al. 2017) trends are attributed to changes in emissions while other studies focus on the influence of the ocean (Chen et al. 2015, Chen et al. 2016). Trends in wet deposition are even more variable. Studies at sites in North America show a combination of increases and decreases that are sensitive to location and the time period of analysis (Weiss-Penzias et al. 2016). For fish concentrations, decreases in the Atlantic (Lee et al. 2016) and increases in the Pacific (Drevnick et al. 2015, Drevnick and Brooks 2017) are both qualitatively linked to global-scale emissions changes. Declines in mercury in open ocean fish will likely begin to decrease within years to decades while mercury in fish from coastal areas contaminated by legacy mercury may take many decades, or even centuries, to decline, due to differences in mercury cycling in these different ecosystems (Chen et al. 2016). Identifying these signals is also complicated by other global changes occurring simultaneously, including climatic changes (Krabbenhoft and Sunderland 2013).

Some research has used information on mercury emissions, cycling, transport and deposition to simulate the health and economic impacts resulting from anticipated policy choices under the Convention. This kind of analysis makes it possible to quantify the relative importance of various sources of uncertainty and variability across the chain of policies-to-impacts when estimating human health and economic impacts of the Convention. Uncertainties in the mercury cycling and ecosystem dynamics that influence the timescale of changes in mercury concentrations have been found to strongly affect benefit estimates (mainly because of time discounting of future benefits) (Giang and Selin 2016).) An economic evaluation of the health benefits of mercury emission controls consistent with Convention implementation in China found mercury-related health benefits >$400 billion by 2030 (Zhang et al. 2017).

Areas For Further Work

Despite extensive scientific efforts to understand the mercury cycle, scientific uncertainties and environmental variabilities challenge the ability to link global changes in emissions and environmental cycling to environmental concentrations and exposures. These obscure the ability to attribute changes due to Convention related implementation measures (Selin 2014b, Kwon and Selin 2016). Any hope of overcoming the difficulties discussed above requires the collection of better empirical data on mercury emissions and concentrations and on relevant environmental factors affecting atmospheric transport and biogeochemical cycling. In addition, the development of a reliable baseline is critical for evaluating the impacts and effectiveness of the Convention. While data are available in many cases (e.g. Global Mercury Assessment) for emissions and releases, they may be lacking for other important variables. Further, political considerations may complicate which information the COP ultimately chooses as baseline.

To address analytical challenges, scientists need to develop new sampling and analytical methods (including methods for quality control of measurements, particularly for oxidized and particulate mercury (Jaffe et al. 2014)), and cost-effective monitoring designs, and will need to dramatically improve models that can make use of such data in robust ways. It is especially critical to develop a better understanding of behavior of mercury in conditions common to tropical regions, where a large proportion of global mercury emissions now occur (United Nations Environment Programme 2013b). In addition, new methods are needed for integrating this scientific information with other social and economic information called for in Article 22, into a coherent framework against which Convention effectiveness can be assessed.

The methods used to collect and analyze monitoring data need to be harmonized (Bank et al. 2014). Experts may recommend concentrating on more comparable, reliable and longer term monitoring in fewer locations, and place greater emphasis on strategic measurements in key human populations and ecosystems, rather than a greater number of measurements (Gustin et al. 2016). Many existing monitoring networks need expansion and enhancement to contribute to such important policy questions (especially in the global South where coverage is sparse, against inevitable resource limitations). One expansion effort concerns the Asia-Pacific Mercury Monitoring Network, which aims to create a coordinated Asia-wide network to monitor mercury transport and deposition. Scientists can guide such efforts, including how to appropriately interpret monitoring data given different spatial and temporal scales of mercury processes in the environment and the non-linear relationship of mercury deposition and biotic methylmercury concentrations.

As noted above, the initial effectiveness evaluation is likely to be informed primarily by assessment of data and models representing beginning and intermediate steps in the causal chain from policies-to-impacts. This approach is generally consistent with the framework for the effectiveness evaluation for the Stockholm Convention on Persistent Organic Pollutants, which includes a series of "outcome indicators" meant to reflect changes in impacts on human health and the environment (United Nations Environment Programme 2017a). An ad hoc expert group is tasked to help determine monitoring network designs suitable for meeting policy needs. The outcome indicators are also complemented by a series of "process indicators" that indicate levels of compliance with control measures and the overall degree of implementation of mandates (United Nations Environment Programme 2013a). A similar set of outcome and process indicators may be developed for the Minamata Convention.

Many of the process indicators must rely on reporting about the implementation of specific control measures, but can also be supplemented by targeted data collection on specific expected outcomes, such as the declining market availability of products to be phased out by 2020 (e.g., certain medical devices, skin-lightening creams). Additional research can build on existing proposals for a suite of such process indicators intended to reflect the effectiveness of five key control provisions (related to trade, products and processes, ASGM and air emissions) in addition to recommending longer-term indicators based on biomonitoring of ecosystems and human populations (Evers et al. 2016). Specific process indicators can be proposed for the short term (less than 6 years), medium term (6-12 years) and long term (greater than 12 years), to match different target dates for the implementation of Convention provisions.

Using a broader definition of "effectiveness," research can strengthen the evaluation by further developing metrics related to changes in underlying social drivers that influence the uses and emissions of mercury. For example indicators can be determined that reflect the increased capacity of scientists, governments and others to manage mercury per Articles 14 and 17. Effectiveness of efforts under Article 18, to raise public awareness of mercury, can be evaluated by how well they have been able to modify cultural and social views among critical target populations whose behavior influences the rate of change of mercury use and emissions. Such changes are hard to quantify, much less directly observe and measure, and will require social scientists such as educators, communication specialists, and program evaluation specialists to develop appropriate indicators (Macdonald et al. 1996, Centers for Disease Control 1999, Abroms and Maibach 2008).

Awareness Raising and Science-Based Education

Several articles of the Convention recognize the importance of raising awareness, strengthening science-based education, and increasing information gathering and exchange. Related to the broader definition of effectiveness evaluation, the collective application of these articles is important to achieve effective treaty implementation among all parties. They are, however, especially important in developing countries where the awareness of the environmental and human health impacts of mercury and the availability of domestic resources for comprehensive mercury management often are limited. To this end, Article 13 on financing and Article 14 of capacity building, technical assistances and technology transfer contain a set of provisions related to the importance of providing assistance to developing countries.

Article 16 calls on parties to promote the development and implementation of strategies and programs to identify populations at risk from mercury exposure, as well as science-based public educational programs. Parties are encouraged to adopt science-based health guidelines relating to mercury exposure and to promote and strengthen health-care services. Article 17 stipulates that parties shall exchange scientific, technical, economic and legal information. This includes information on the reduction or elimination of the production, use, trade, emissions and releases of mercury; information about technically and economically viable alternatives for mercury use in products and processes; and epidemiological information concerning mercury-related health impacts. Article 18 states the parties shall promote and facilitate public information, awareness and education.

Existing Knowledge

Research shows that efforts to build capacity for implementation of other treaties benefits from concerted efforts across global, regional, national and local governance scales (Selin 2010). In these cases, the Secretariat plays an important global role in collecting, publishing and disseminating data (Jinnah 2014). The Minamata Convention Secretariat works alongside major IGOs, including UN Environment, the World Health Organization, United Nations Development Programme and the United Nations Industrial Development Organization, in hosting and supporting regional capacity building programs and training sessions that promote information exchange, including helping to prepare country's treaty ratification and implementation. Stockholm Convention and Basel Convention regional centers working with countries on capacity building and technology transfer issues on a regional basis address mercury management issues (Selin 2012, United Nations Environment Programme 2016).

Studies and on the ground experiences from the Global Mercury Partnership and other initiatives demonstrate that the design and implementation of effective awareness raising and science-based education programs require a comprehensive and long-term approach, and efforts must be flexible enough so that they can be adjusted over time and be tailored to specific local legal, political, economic, social, cultural and environmental contexts (Chouinard and Veiga 2008, Sousa and Veiga 2009, United Nations Development Programme 2009, Arctic Monitoring and Assessment Programme 2015). It is important that efforts to disseminate information and new methods and technology to change the behavior of targeted groups include close and repeated interactions between authorities, experts and community members (García et al. 2015). Many of the more effective efforts also target key individuals whose actions and choices will heavily influence the decisions by others and outcomes of community-wide efforts to change attitudes and behaviors (Sippl and Selin 2012).

Scientific and technical knowledge is key to efforts to change attitudes and behavior among particularly vulnerable populations, and this is especially true in the ASGM sector. Studies show that reductions in mercury use and exposure should comprise both the dissemination of science-based information on the environmental and health risks from mercury as well as working with miners to develop and apply new technologies for reducing mercury emissions and exposure (Zolnikov 2012). Also, inducing miners to shift to mercury-free techniques requires more than a demonstration of alternative technologies; it takes an understanding of local socio- economic and cultural factors and relationships among different actors along the gold supply chain. In addition, much ASGM takes place in the informal sector, creating a host of legal, political and management challenges (Hilson and Gatsinzi 2014).

Dentistry is another major area of intentional mercury use where there are efforts to generate and communicate science-based information for behavioral change. For example, a civil society initiated campaign to phase down the use of mercury amalgams in Asia and Africa faced initial resistance from policy makers and dentists who did not believe that mercury posed a risk. To overcome this skepticism, scientists from several countries in both regions used a portable device to measure mercury levels in air in dental offices (Ali and Khawja 2015). Such on-the-spot measurements demonstrating high mercury levels were a strong method of direct risk communication with dentists while considering national cultural differences, and helped garner support for changing workplace practices to reduce exposure. The findings were also supported by a WHO publication and other studies (World Health Organization 2010, Ferracane 2011).

Studies also seek to identify the scope of the problem with methylmercury in fish in different species and regions, raise awareness, and communicate appropriate dietary guidelines, especially for vulnerable populations such as pregnant women and small children (Mergler et al. 2007, Mahaffey et al. 2011). In developing science-based guidelines, it is critical that experts work closely with local communities, including indigenous communities where the harvesting and consumption of seafood are integral to long-standing cultural values and practices (Arctic Monitoring and Assessment Programme 2015). It is important that nutritional benefits of fish consumption are evaluated against risks of mercury exposure when designing consumption guidelines (Mahaffey et al. 2011). Consumption related research also focuses on mercury in rice, as some rice in China is grown in mercury-contaminated paddy fields (Li et al. 2009, Rothenberg et al. 2014).

Areas For Further Work

The ability to meet Convention goals and commitments depends on recognizing political, economic, social and cultural dimensions of collective and individual actions in the context of highly complex coupled human-natural systems. Improving programs for awareness raising and the generation and communication of science-based information to change human behavior requires research on risk communication in different knowledge systems. It requires the expertise of specialists and educators to use different communication tools and craft effective messages tailored to local communities, policy makers and the general public (Arctic Monitoring and Assessment Programme 2015). Efforts to design better science-based awareness raising and risk description and communication in turn are dependent on improved quality and quantity of mercury biomonitoring data for different species and ecosystems as well as health effects of low-level exposure to different human populations (Arctic Monitoring and Assessment Programme 2015).

Many collaborative efforts on science-based education and awareness raising will continue to focus on the ASGM sector, as the totality of past and current initiatives across South America, Africa and Asia have not been enough to adequately address the problem of related mercury emissions and releases and dangers posed to local communities and environments. To better understand these risks, more empirical research is needed on emissions, releases and environmental cycling of mercury from ASGM and exposures to miners and their communities (including urban processing centers). To then meet the goals of reducing or eliminating mercury use and minimize health impacts, it is necessary to refine existing technologies and/or develop new mining methods, and to work with individual miners to introduce them. To fulfill longer-term goals of moving to mercury-free mining there is a need to further explore opportunities for alternative livelihoods and collaborate with mining communities, local and national governments and international organizations in support of sustainable development. This often requires the establishment of greater trust between experts and miners and other community members.

Importantly, efforts to expand the introduction of mercury-free techniques in ASGM communities must consider the social and economic drivers of the use of mercury in order to see more widespread uptake of new methods and technologies. For example, some miners use mercury despite the better efficiency of other technologies because mercury-based approaches allow them to produce income on a daily basis while others disdain centralized processing because of a lack of trust between miners and processors.

Related, there is a need to further develop and apply performance indicators to evaluate education and technology diffusion programs (Sousa and Veiga 2009).

Further research can assist efforts to phase out the use of mercury and mercury-containing products, taking into consideration both scientific information and local conditions. This includes working with dental professionals and patients to reduce the use of mercury amalgam as well as assuring medical practitioners about the efficacy of mercury-free alternatives to existing mercury thermometers and sphygmomanometers. Educational campaigns in Africa discovered that women still use mercury-containing skin lightening products because women with fair skin are perceived to be more attractive by prevailing social standards (Agorku et al. 2016). Because of these social pressures, legislation in several countries against these products has been difficult to implement. In addition, there are continuing needs for localized research to examine health risks from dietary intake of mercury-containing food, including fish and rice, and devise appropriate consumption guidelines for different communities (Meng et al. 2014, Arctic Monitoring and Assessment Programme 2015).

The Future of Mercury Science and Governance

The Minamata Convention is set to play a central role in environmental and human health protection from mercury-related exposures and risks. The most recent effectiveness evaluation of the Stockholm Convention on POPs notes that an environmental treaty also can act as an important catalyst for expanded research, monitoring, and modeling and for bringing together findings from different parts of the world (United Nations Environment Programme 2017b). Future mercury research can support convention implementation efforts in numerous ways and feed into policy-making and management at multiple times and entry points. This article's earlier discussion should not be seen as exhaustive of all the areas and ways in which the larger research community can contribute, but rather as an effort to further connect research opportunities with convention implementation needs. Here, there is a high demand for interdisciplinary expertise and perspectives.

As the parties move forward under the Convention, building on work carried out under the Global Mercury Partnership and other programs, there is a need to strengthen multilevel approaches to mercury management across global, regional, national, and local governance scales (Selin 2014a). Governance focused studies can continue to analyze how activities and decisions in different fora and governance levels by international organizations, countries and civil society organizations are linked, and explore ways in which such linkages can be used to create synergistic effects toward better mercury management. Such studies should be carried out alongside more research into the impacts of mercury on human health and the environment and how mercury cycles through different environmental media, because better mercury management is dependent on a combination of scientific information from different sources, fields, and disciplines.

To enable different forms of continued applied mercury-related research in support of policy-making, it is important to build and support basic scientific and analytical capabilities. This is especially true for developing regions of the world where scientific capacity building and technology diffusion are central issues. Developing and newly industrialized countries are also likely to be the ones where the most wide-ranging policy measures are needed. This includes major cuts in atmospheric mercury emissions from coal-fired power plants and other major stationary sources, the phasing out mercury use in products and processes, and reducing and ultimately eliminating mercury use in ASGM. Building implementation capacities in these countries and supporting technology transfer will be critical to the success of the Convention.

This synthesis paper focuses mainly on scientific contributions to the implementation of existing treaty provisions. However, as the COP oversees the implementation, including through the use of the facilitative compliance mechanism (Templeton and Kohler 2014), provisions will be reviewed and some may be amended. For example, the COP may identify other sources of mercury emissions and releases as well as update BAT and BEP guidance. Also, the introduction of stricter BAT and BEP controls on stationary sources will result in more mercury captured before being released, which can result in more mercury going into solid and liquid wastes increasing the need for waste management. In addition, the COP may expand focus to additional mercury-containing products and processes. On all such decisions, the COP will benefit from additional scientific and technical information.

The implementation of the Convention also intersects with other environmental treaties. A greater attention to mercury wastes creates stronger linkages with the Basel Convention (Selin 2010), which is directly connected to the Minamata Convention in Article 11. Climate change has implications on mercury pollution and its impacts (Arctic Monitoring and Assessment Programme 2015). For example, climate-induced changes in food web structures may enhance bioaccumulation and biomagnification of methylmercury in some marine species (Jonsson et al. 2017). In addition, mercury management takes place in a broader context of the sustainable development agenda, linked to Sustainable Development Goals on good health and well-being, clean water and sanitation, affordable and clean energy, responsible consumption and production, and sustainability of life below water.

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A review of global environmental mercury processes in response to human and natural perturbations: changes of emissions, climate and land use

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DRAFT June 28, 2017

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Abstract/Summary

We review current knowledge of important processes for the global distribution of mercury (Hg), including recent research advances, current uncertainties, and best estimates of concentrations and pools sizes in the atmospheric, terrestrial, and aquatic environments. Recent advances include the availability of new global datasets with measurements that now cover areas of the world where previously environmental Hg data were lacking. Integration of such data into global and regional models are continually improving estimates of global Hg cycling. Hg stable isotope techniques now provide valuable tools to quantify Hg sources, study transformation processes, and help constrain the relative importance of specific sources and transformation in the global context. Key uncertainties in the global cycling of mercury are related to exchange processes between the atmosphere, terrestrial, and aquatic ecosystems; atmospheric dry deposition including plant uptake, re-emissions, and oxidation processes; methylation and demethylation particularly in oceans; and residence and turnover times in terrestrial and aquatic environments.

A key conclusion of our synthesis is that in addition to past Hg enrichments in all environmental compartments as a result of anthropogenic activities, large impacts are now observed due to global change. We highlight a series of recent studies that show ongoing changes and project anticipated effects of future changes in emissions, climate change, and land use change on the global fate of Hg. Such changes will be large and strongly depend on changes in ecosystem function and atmospheric and ocean circulations. Current uncertainties limit our ability to predict future global cycling and therefore human exposure, in particular when there are multiple and simultaneous changes occurring. Finally, we close with recommendations for research needed to reduce key uncertainties.

1. Introduction and current global pool size estimates of mercury

The goal of this synthesis paper is to summarize recent progress on understanding critical processes of global importance for mercury (Hg) cycling, in particular processes and pathways that affect large-scale exchange of Hg among major environmental compartments. We also summarize current estimates of global pool sizes in the atmosphere as well as terrestrial and aquatic ecosystems, particularly as data have become available from areas of the world where previously environmental Hg data was rare or lacking – including from Asia, the Tropics, and the Southern Hemisphere. Increasing spatial data coverage via new data sets showing landscape gradients and hemispheric patterns as well as global data assimilation studies allow for better global analysis of important drivers such as climate and ecosystem properties, circulation patterns, plus anthropogenic and natural emissions. Environmental models are increasingly used for synthesizing global observations and best-available understanding of mechanisms driving Hg speciation, cycling, and bio-availability. Global 3-D modeling has been focused on compartment specific analyses (i.e., the atmosphere) that use boundary conditions for other components of the global ecosystems (e.g., terrestrial-atmosphere exchange, air-sea exchange). Examples include atmospheric (Dastoor and Larocque 2004, Selin et al. 2007, Jung et al. 2009, Travnikov and Ilyin 2009, Holmes et al. 2010, Durnford et al. 2012, Bieser et al. 2017), terrestrial (Smith-Downey et al. 2010), and ocean models (Zhang et al. 2014, Zhang et al. 2015b, Semeniuk and Dastoor 2017). These models are computationally expensive to run and thus long-time-scale simulations with full representation of each compartment are currently not feasible. A major advance has been the development of a hierarchy of modeling tools that collapses the necessary detail from these global simulations into more simplified geochemical box models (Amos et al. 2013, Amos et al. 2014, Amos et al. 2015). This allows for a fully-coupled simulation of the interactions among the land, atmosphere, and oceans using all-time emission estimates from bottom-up inventories (Streets et al. 2011, Streets et al. 2017). When process-based model simulations disagree with observations, researchers gain new insights on incomplete understanding and gaps in available knowledge. When models successfully reproduce observations, results can be useful for extending observations in space and time, and also for informing decision makers on potential outcomes associated with different regulatory interventions such as emission controls (synthesis paper 4 (Selin et al. 2017). An important application for Hg modeling also is to evaluate policy efforts to mitigate Hg pollution (Selin 2014).

The potential for models to project observations and impacts through time is particularly valuable when investigating anticipated impacts of human and natural perturbations on global Hg cycling. Changes in anthropogenic emissions are ongoing and will continue to take place in the future, including strong shifts in source areas globally compared to current emission patterns (Giang et al. 2015). The world is undergoing accelerating land use and climate change – including increases in ocean and air temperatures, with air temperatures warming above 1.5°C by 2100 relative to 1850 to 1900; higher precipitation contrasts between wet and dry regions; shrinking Arctic sea ice cover and decreasing spring snow cover; and changes in carbon cycling that will exacerbate the increase of atmospheric CO_2 and ocean acidification (IPCC 2013). The effects on global, regional, and local Hg cycles will be significant with unexpected feedbacks and nonlinear impacts on Hg exposure. An increasing number of studies are now available documenting such changes, and we will review some key reported responses. This synthesis effort focuses on processes of Hg cycling of global importance and perturbations thereof. More detailed discussion of factors specifically affecting aquatic mercury loading, methylation and demethylation processes, and exposure of wildlife and humans to Hg in the context of environmental change and disturbances are provided in synthesis papers 2 and 3 (Eagles-Smith et al. 2017, Hsu-Kim et al. 2017).

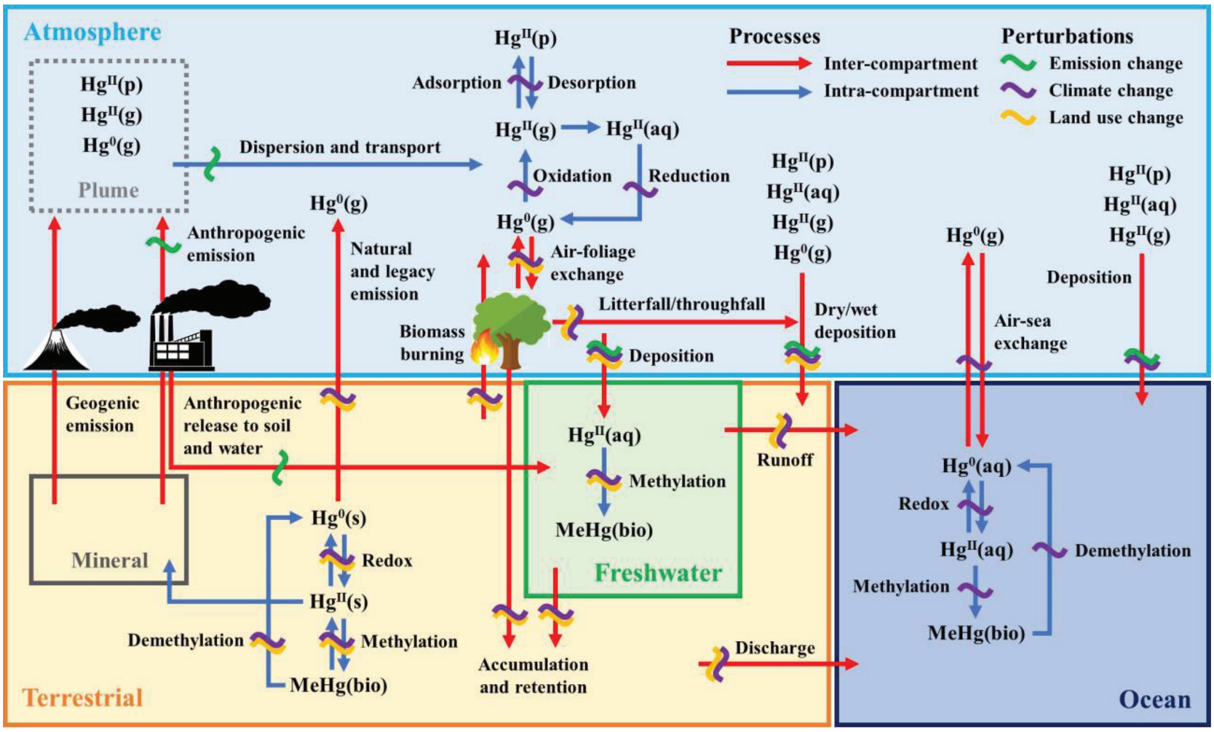

Figure 1: Schematic diagram highlighting critical processes of global importance for Hg cycling – including fluxes between major global reservoirs and environmental compartments. Perturbations of Hg processes and fluxes show anticipated impacts due to emission, climate, and land use changes. Detailed discussion of the relevant processes is found in section 2, and major disturbances to global Hg cycling are discussed in section 3.

We first provide a short overview of globally relevant Hg pool sizes and modern anthropogenic impacts. ***In the atmosphere***, mean total gaseous mercury (TGM) concentrations in the Northern Hemisphere, the Tropics, and the Southern Hemisphere are 1.3–1.6, 1.1–1.3, and 0.8–1.1 ng m^{-3}, respectively (Slemr et al. 2011, Sprovieri et al. 2016). Atmospheric TGM concentrations have been measured since the late 1970s with more reliable observations emerging since ~1990 (Slemr et al. 2003, Lindberg et al. 2007, Temme et al. 2007, Sprovieri et al. 2010, Slemr et al. 2011, Sprovieri et al. 2016). Many observations show that in the past three decades, global background TGM concentrations have declined, particularly in North America, Europe, and over the North Atlantic Ocean (Slemr et al. 2003, Lindberg et al. 2007, Temme et al. 2007, Slemr et al. 2008, Ebinghaus et al. 2011, Slemr et al. 2011, Soerensen et al. 2012, Cole et al. 2013, Weigelt et al. 2015, Sprovieri et al. 2016). Proposed drivers for such declines include decreased Hg concentrations in the upper North Atlantic Ocean and/or changes in terrestrial emission rates (Slemr et al. 2011, Soerensen et al. 2012). Others showed that declining emissions of divalent Hg (Hg^{II}) in the Northern Hemisphere and from commercial products (Horowitz et al. 2014) were sufficient to reproduce observed declining trends from 1995 to present (Zhang et al. 2016d). TGM concentrations have decreased at lower rates in parts of the Arctic (~0 to -2 % yr^{-1}) (Cole et al. 2013). Several studies have suggested a recent reversal in global TGM trends because of rising emissions from coal-fired power plants in China and India plus artisanal and small-scale gold mining (ASGM) activity (Slemr et al. 2014, Martin et al. 2017, Streets et al. 2017). At Cape Point in South Africa, TGM has increased during the last decade, although a clear explanation for this trend is lacking (Martin et al. 2017).

The current global atmospheric Hg reservoir is estimated at between 4600 and 5300 Mg and is enriched more than five-fold relative to natural levels and by about three-fold relative to 1850 (Amos et al. 2013, Engstrom et al. 2014, Horowitz et al. 2017, Streets et al. 2017). Impacts of anthropogenic contributions on atmospheric Hg loads and deposition have also been inferred from observations in polar firn air, peat bogs, and lake sediments – all revealing large-scale impacts of anthropogenic emissions, particularly in the second half of the 20th century (Faïn et al. 2009, Farmer et al. 2009, Outridge et al. 2011, Goodsite et al. 2013, Engstrom et al. 2014, Amos et al. 2015, Blais et al. 2015, Drevnick et al. 2016). A recent combination of deposition records with Hg stable isotope analysis now allows differentiation between Hg^{II} and Hg^0 deposition, and reconstruction of past GEM levels (Enrico et al. 2016, Enrico et al. 2017). Enrico et al. (2017) suggest that maximum 20th century Hg^0 concentrations were 15 times larger than natural background at the sampling locations. Reconstructions suggest that historical atmospheric Hg^0 concentrations peaked around 1970 at 3–4 ng m^{-3} and declined subsequently to current levels of 1.3–1.6 ng m^{-3} (Faïn et al. 2009, Enrico et al. 2017), in agreement with atmospheric Hg^0 concentration measurements of the last decades. Lake sediment archives, reflecting total atmospheric Hg deposition, show similar time trends with maximum Hg accumulation rates around 1970-1990 (Engstrom et al. 2014, Amos et al. 2015, Drevnick et al. 2016). Decreasing atmospheric Hg^0 concentrations since the 1980's have now been associated with declining trends in Hg levels in ocean fish (Cross et al. 2015, Lee et al. 2016) and in litterfall forest deposition (Gerson and Driscoll 2016).

In the terrestrial environment, the largest Hg pools are located in soils (Grigal 2003, Obrist 2012) which in the upper horizons are derived predominantly from exogenic, atmospheric inputs (Grigal et al. 2000, Schwesig and Matzner 2000, Guedron et al. 2006, Peña-Rodríguez et al. 2012, Demers et al. 2013, Peña-Rodríguez et al. 2014, Jiskra et al. 2015, Enrico et al. 2016, Zheng et al. 2016, Wang et al. 2017). Atmospheric Hg inputs are strongly retained in humus-rich upper soils bound to organic matter (Meili 1991, Grigal 2003, Obrist et al. 2011, Jiskra et al. 2015). A component of soil Hg also stems from natural, geologic sources. Using global soil carbon inventories, global soil Hg pools have been estimated at 300 Gg (Hararuk et al. 2013) and 240 Gg (Smith-Downey et al. 2010), showing an estimated ∼20% modern- day increase compared to preindustrial pools of 200 Gg (Smith-Downey et al. 2010). Upper soil pools with higher turnover rates may be enriched several-fold relative to natural levels, however (Smith-Downey et al. 2010, Amos et al. 2013). Newer simulations using additional observational constraints and all-time releases for Hg from human activity (Streets et al. 2011, Horowitz et al. 2014) estimate present-day organic soil Hg pools even higher (250 to 1,000 Gg with a best estimate of 500 Gg) and propose that anthropogenic emissions have doubled the Hg pool stored in organic soils (Amos et al. 2013, Amos et al. 2015). Hg pools contained in vegetation account for ~1% of total ecosystem pools (Obrist 2012), but Hg in vegetation represents a highly dynamic pool that is critical for terrestrial cycling as it dominates deposition in most terrestrial ecosystems (section 2B).

Oceans contain a substantial fraction of the global Hg reservoir and strongly affect atmospheric concentrations through air-sea exchange (Mason and Sheu 2002, Strode et al. 2007, Sunderland and Mason 2007, Soerensen et al. 2010). Sunderland and Mason (2007) estimated total ocean Hg to be 350 Gg with a 90% confidence limit of 270–450 Gg. More recent work (Lamborg et al. 2014, Zhang et al. 2015b) suggests a reservoir of 260–280 Gg. Lamborg et al. (2014) estimated the upper ocean (top 1000 m) reservoir based on observations from the GEOTRACES cruise series at 63 Mg, which is on the low end of the range reported in Sunderland and Mason (2007) (63–120 Mg; 90% confidence interval) and may indicate declining concentrations in some basins or improvements in analytical techniques (Lamborg et al. 2012). In the pelagic marine environment, trends in total Hg concentrations (THg) are difficult to infer because of large inter-laboratory variability in measurements (Lamborg et al. 2012). Concentrations in the North Atlantic appear to be continuing to decline during the last several decades, from mean vertical profile concentrations of above 5 pM in the 1990s to consistently below 1 pM on recent cruises (Bowman et al. 2016). In the North Pacific, however, Sunderland et al. (2009) suggest that THg concentration in the North Pacific Intermediate Water (NPIW) mass has increased since the mid-1980s from enhanced atmospheric inputs from the Asian continent. More recent studies (Hammerschmidt and Bowman 2012, Munson et al. 2015) did not see statistically different concentrations than those measured on earlier cruises, although data coverage was sparse.

In freshwater ecosystems, predominant Hg sources include direct discharge of Hg-containing effluents, runoff/rivers that contain high amounts of atmospheric Hg that accumulated in terrestrial environments, and direct atmospheric deposition that is particularly important in lakes with large surface area to volume ratios and small catchment to lake surface area. The relative importance of atmospheric and watershed sources varies (section 2C and synthesis paper 2 (Hsu-Kim et al. 2017)), depending on the degree of development and land-use change, hydrology, and dissolved organic carbon (DOC) content and composition (Engstrom and Swain 1997, Knightes et al. 2009, Lepak et al. 2015). Kocman et al. (2017) recently developed the first inventory of Hg releases to freshwater ecosystems and estimated 800–2200 Mg yr^{-1} of Hg enters freshwater ecosystems, with ASGM as the largest contributor globally. This is lower than the amount of Hg entering coastal ecosystems estimated by Amos et al. (2014) (5500 ± 2700 Mg yr^{-1}) based on a review of global concentration data and gridded data on particulate loads and aquatic discharges from rivers globally, in part because it does not include natural discharges from terrestrial ecosystems. Earlier estimates of global riverine discharges to the ocean were between 1000 and 2000 Mg yr^{-1} (Cossa et al. 1997, Sunderland and Mason 2007); they did, however, not account for highly elevated concentrations recently observed in Chinese rivers (Amos et al. 2014), although these may require further observational constraints. Streets et al. (2017) constructed the first all-time emissions inventory for global Hg releases from human activity, including releases to land and water, and suggest ~40% of land/water releases globally are sequestered at the release site rather than traveling in rivers to the ocean.

2. Recent advances in understanding critical Hg cycling processes of global importance

A. Atmosphere

Anthropogenic Emissions*:* Anthropogenic Hg emissions account for ~30% of total annual emissions (Pirrone et al. 2010, UNEP 2013, Streets et al. 2017). While several different emissions inventories exist for the present day, fewer are comparable across the past decades (Muntean et al. 2014), and only one addresses all-time human emissions (Streets et al. 2011). Global anthropogenic Hg emissions have been estimated in the range of 2000 Mg yr^{-1} by most studies (AMAP/UNEP 2008, Pacyna et al. 2010, Pirrone et al. 2010, Streets et al. 2011, AMAP/UNEP 2013) except one lower estimate (EDGARv4) of 1287 Mg yr^{-1} (Muntean et al. 2014). While reference years of studies are within a common period of 2005–2010, the sectoral distributions among studies are inconsistent. AMAP/UNEP (2008) and studies by Pacyna et al. (2010), Pirrone et al. (2010) and Streets et al. (2011) found stationary fossil fuel combustion (SFFC), mainly coal combustion, to be the leading source (800–900 Mg yr^{-1}), followed by ASGM (400 Mg yr^{-1}). By assuming a higher activity level of unregulated and illegal ASGM in some countries, UNEP's 2013 global Hg assessment (AMAP/UNEP 2013) estimated more than 700 Mg yr^{-1} for ASGM emissions. SFFC accounted for less than 500 Mg yr^{-1} in the UNEP inventory, while the EDGARv4 inventory (Muntean et al. 2014) estimated both SFFC and ASGM to be lower.

National-level emission inventories rely on local field emission tests with increasing data now emerging from newly industrialized countries. For example, Zhang et al. (2015a) estimated anthropogenic Chinese emissions for 2010 of 538 Mg, which is lower than a previous estimate of 609 Mg yr^{-1} (Pirrone et al. 2010). The discrepancy was attributed to better Hg removal efficiencies of air pollution control devices for non-ferrous metal smelting (Wang et al. 2010, Zhang et al. 2012). Indian emissions were recently estimated at

~240 Mg yr^{-1} (Pirrone et al. 2010, Burger Chakraborty et al. 2013). National anthropogenic Hg emission estimates also are available for other countries (Kim et al. 2010, Masekoameng et al. 2010, Nansai et al. 2012, Nelson et al. 2012, US EPA 2015). Per the UNEP emission inventory, the seven highest emitting countries are (in order) China, Indonesia, Columbia, South Africa, Russia, Ghana, and the U.S. – with these countries emitting a total of 1015 Mg yr^{-1}, or 54% of global anthropogenic emissions to the atmosphere (UNEP 2013). More accurate emission inventories are expected in the future, as parties of the UNEP Minamata convention on Hg are required to improve national Hg use and emission inventories.

Uncertainties in the global anthropogenic Hg emission inventory are mainly because of lack of local field test data for key sectors – such as cement production, iron and steel production, waste incineration, gold production, including from China and India; and lack of accurate activity-level data for ASGM and intentional Hg use. Horowitz et al. (2014) found that more than 400 Mg yr^{-1} of atmospheric Hg emission was from intentional use of Hg in products and processes (excluding gold production), that was previously overlooked. Top-down constraints and inverse modeling from atmospheric observations were recently used to verify emission inventories (Song et al. 2015, Song et al. 2016, Denzler et al. 2017). Finally, Hg speciation profiles of emissions are crucial to assess environmental impacts of atmospheric emissions (Zhang et al. 2016b). For example, Streets et al. (2005) used the overall Hg^0:Hg^{II}_{gas}:$Hg^{II}_{particulate}$ ratios of 20:78:2 and 80:15:5 for Chinese coal-fired power plants (CFPPs) and cement plants (CPs), respectively, based on North American and European field test data. A recent study by Zhang et al. (2015a) updated the speciation profiles to 79:21:0 and 34:65:1 for Chinese CFPPs and CPs, respectively, based on onsite measurements. Such changes in speciation profiles for large point sources will lead to large variations of Hg transport distances and local deposition fluxes.

Terrestrial Hg emissions to the atmosphere: Atmospheric emissions of Hg^0 from terrestrial ecosystems were originally estimated to be very high (Selin et al. 2008, Smith-Downey et al. 2010) but more recent estimates are considerably lower. Large terrestrial Hg^0 emissions – or legacy emissions of previous depositions –were in part based on the METAALICUS isotope tracing study that showed that 45–70% of applied labile $HgCl_2$ was subject to atmospheric re-emission (Graydon et al. 2012). Recent global data assimilations of 20+ years of terrestrial Hg^0 flux measurements (Agnan et al. 2016, Zhu et al. 2016) now show that in most of the world, Hg^0 evasion from background soils is generally low, particularly when soils are covered by litter or plants, but also highlight large uncertainties in terrestrial Hg^0 emission and deposition rates. Discrepancies between high rates of revolatilization of Hg^{II} added in the METAALICUS study (Graydon et al. 2012) and low rates of Hg^0 emissions measured in remote field studies may be linked to the different chemical forms of deposition (Hg^0 versus Hg^{II}; section 2B). In fact, many background soils also show periods of net Hg^0 deposition (Gustin et al. 2000, Choi and Holsen 2009) with recent work showing net Hg^0 deposition in 20% of measurements over bare soils and in 45% of covered soils (Agnan et al. 2016). On the other hand, Agnan et al. (2016) and Zhu et al. (2016) showed the increased importance of soil Hg^0 emissions in areas with high atmospheric Hg exposures (such as East Asia, e.g. (Fu et al. 2012, Sommar et al. 2016)), that according to Agnan et al. (2016) globally account for 261 Mg yr^{-1} (range of 114–359 Mg yr^{-1}) and constitute the largest terrestrial Hg^0 source. They also estimated lower Hg^0 emissions from naturally Hg-enriched and contaminated areas (i.e., 217 Mg yr^{-1}, range of 202–258 Mg yr^{-1}), lower compared to previous estimates (Ericksen et al. 2006) but still the second largest terrestrial Hg^0 source. Another significant terrestrial Hg^0 emission source is global croplands (201 Mg yr^{-1}; range 195–208 Mg yr^{-1}). When considering vegetation uptake, terrestrial ecosystems turn into net atmospheric Hg^0 sinks, estimated at net Hg^0 deposition of 59 and 89 Mg yr^{-1} in global forests and grasslands, respectively. Current uncertainties related to vegetated ecosystems based on Hg^0 flux measurements, however, are large (e.g, showing a range from net deposition of 727 Mg yr^{-1} to net emission of 703 Mg yr^{-1} across global forests). Recent global model simulations now reflect reduced terrestrial Hg^0 losses (Amos et al. 2014, Amos et al. 2015), with a recent global atmospheric model simulation (Song et al. 2016) reducing global soil emissions from 2200 Mg a^{-1} to 1360 Mg yr^{-1}, still much larger than estimated by Agnan et al. (2016). The current large uncertainties in terrestrial Hg^0 sinks and source strengths, particularly over background areas and vegetated areas, make this term one of the largest uncertainties in the global Hg cycle. Also, modeling studies use an estimate of 76±30 Mg yr^{-1} of geogenic emissions based on Bagnato et al. (2014).

Biomass burning: Recent global atmospheric Hg models include global biomass burning emissions between 210 and 680 Mg yr^{-1} (Amos et al. 2014, De Simone et al. 2015, Song et al. 2016). While wildfire emission in large parts can be considered as a natural process re-cycling Hg between the atmosphere and terrestrial ecosystems, climate and land use change impacts induced by anthropogenic activities, including increased fire frequency and activity (Westerling et al. 2006) need to counted as human impacts on Hg cycling. In addition, land management practices such as burning of agricultural fields, grassland, and brush fires contribute to additional Hg emissions, although little information is available on their global contribution. Webster et al. (2016) recently provided an update on fire-induced atmospheric Hg losses from western U.S. wildfires and suggest a five-fold lower emission total (3.1 ± 1.9 Mg yr^{-1} across 11 states) compared to previous estimates (14.7 Mg yr^{-1}) (Wiedinmyer and Friedli 2007). Webster et al.'s lower emission estimates are attributed mainly to inclusion of fire severity and the notion that low severity burns (52% of wildfires) result in lower soil heating and Hg emissions. Other studies also found that Hg losses relate to fire intensity (Mitchell et al. 2012, Kolka et al. 2017). Wildfire studies consistently show that fires mobilize Hg primarily from biomass, litter, and organic soils (Friedli et al. 2001, Friedli et al. 2003, Engle et al. 2006, Biswas et al. 2007, Obrist 2007, Wiedinmyer and Friedli 2007, Biswas et al. 2008, Burke et al. 2010, Woodruff and Cannon 2010), although Hg can be released from upper mineral soils (as much as 10% of total emissions) (Biswas et al. 2007, Burke et al. 2010, Melendez-Perez et al. 2014). Significant post-fire soil evasion losses recently have been reported to occur during years after fires (e.g., leading to an additional 50% of emissions; (Melendez-Perez et al. 2014), an effect which is not included in wildfire emission estimates.

Aquatic Hg^0 emissions to the atmosphere: Air-sea exchange of Hg^0 is critical to extending the lifetime of anthropogenic Hg in the atmosphere, terrestrial ecosystems, and the ocean (Strode et al. 2007, Soerensen et al. 2010). The magnitude of net Hg^0 evasion from the ocean is ~2900 Mg yr^{-1} (range 1900–4200 Mg yr^{-1}) (Horowitz et al. 2017, Streets et al. 2017), compared to ~2000 Mg yr^{-1} from primary anthropogenic emissions and hence is considered the largest source of atmospheric Hg globally. There is, however, substantial uncertainty in the magnitude of air-sea exchange from different ocean regions. Concentrations of dissolved Hg^0 across latitudinal gradients in both the Atlantic and Pacific Oceans show a distinct spike in concentrations around the Intertropical Convergence Zone (ITCZ), hypothesized to result from deep convection and intense precipitation in these regions increasing atmospheric Hg^{II} deposition (Soerensen et al. 2014). Recent data on air-sea exchange are also available for the Pacific Ocean and are in the same ranges as previous cruise data (Mason et al. 2017). Using high frequency measurements of atmospheric and aquatic Hg^0 concentrations, Soerensen et al. (2013) inferred that terrestrial DOC can inhibit Hg^{II} reduction and ambient Hg^0 production in seawater. Lamborg et al. (2016) measured concentrations of Hg on settling organic particulate matter in the Atlantic Ocean and suggested partitioning to particles may be up to 1000 times greater than assumed in some models. This would effectively lower the magnitude of the global evasion flux of Hg^0 from the ocean because scavenging of Hg from surface waters reduces the pool of Hg^{II} available for reduction and conversion to Hg^0.

Atmospheric redox chemistry: Hg^0 oxidation to Hg^{II} is considered key to removing Hg from the atmosphere (Selin et al. 2008, Lyman and Jaffe 2011, Subir et al. 2011), although increasing evidence shows that oxidized Hg^{II} deposition is only dominant to oceans while Hg^0 deposition dominates in terrestrial ecosystems (see below). Recently, there has been much discussion about measurement techniques and artifacts when measuring atmospheric Hg oxidation and atmospheric Hg^{II} concentrations. We refer to published reviews on atmospheric Hg and Hg^{II} methodologies (Lyman et al. 2010b, Jaffe et al. 2014, McClure et al. 2014, Gustin et al. 2015, Mao et al. 2016, Marusczak et al. 2017).

Regarding the oxidation of Hg^0, earlier work suggested a primary role for the oxidants OH and O_3, but recent observations and theoretical calculations suggest that the Br radical is likely the dominant oxidant (Hynes et al. 2009, Gratz et al. 2015, Shah et al. 2016). The mechanism is likely a two-step oxidation process where Hg^0 reacts with the Br radical to form HgBr, and HgBr reacts with all types of oxidants (Br, I, OH, BrO, IO, NO_2, etc.) to generate different Hg^{II} species (Horowitz et al. 2017). This has become the mainstream theory to explain most atmospheric Hg oxidation (Goodsite et al. 2004, Dibble et al. 2012, Wang et al. 2014, Ye et al. 2016, Horowitz et al. 2017, Jiao and Dibble 2017). Recent aircraft observations (Gratz et al. 2015) showed substantial atmospheric Hg^{II} concentrations and detectable BrO in the subtropics, suggesting that subtropical anticyclones are significant global sources of Hg^{II} (Gratz et al. 2015). Interestingly, Shah et al. (2016) utilized GEOS-Chem model sensitivity analysis to show that modeled Hg^{II} concentrations were a factor of three too low and suggested underestimation of the Hg0–Br reaction rate or Br concentrations in models, which has been taken into account recently in GEOS-Chem with updated experimental data and mechanism (Horowitz et al. 2017). This oxidation chemistry was recently updated in the model by Horowitz et al. (2017) based on best available kinetic data from laboratory experiments. In-cloud Hg^{II} photoreduction also may be important in Hg redox chemistry (Holmes et al. 2010, Horowitz et al. 2017). A recent model intercomparison (Travnikov et al. 2017) showed that models with a Br oxidation mechanism reproduced observed near-surface seasonal variation of HgII fraction, but did not capture seasonal variation in wet deposition observed at monitoring sites in North America and Europe. They suggest that more complex chemistry and multi-oxidation pathways may be occurring in different regions of the atmosphere.

Atmospheric Deposition: At background sites, mean atmospheric Hg wet deposition globally likely decreased from 10–15 μg m^{-2} yr^{-1} in the early 1990s to current levels of 5–10 μg m^{-2} yr^{-1} (Zhang et al. 2016d). Wet deposition exhibits larger spatial and temporal variability, however, which complicates trend analyses (Butler et al. 2008, Prestbo and Gay 2009, Risch et al. 2012b, Zhang and Jaeglé 2013, Cole et al. 2014, Muntean et al. 2014, Sprovieri et al. 2016). Extensive monitoring networks exist for measurement of atmospheric Hg^{II} wet deposition, including the Mercury Deposition Network (MDN) for the U.S. and Canada (Prestbo and Gay 2009, Weiss-Penzias et al. 2016) (Sprovieri et al. 2017), the European Monitoring and Evaluation Programme (EMEP) for Europe (Tørseth et al. 2012), a new Asia-Pacific Mercury Monitoring network (APMMN 2017), and the Global Mercury Observation System (GMOS) for the rest of the world. Mean background Hg wet deposition fluxes in the Northern Hemisphere, the Tropics, and the Southern Hemisphere are ~ 5–10, 2–8, and 1–5 μg m^{-2} yr^{-1}, respectively (Prestbo and Gay 2009, Fu et al. 2016a, Sprovieri et al. 2016, Sprovieri et al. 2017). Estimated median dry deposition fluxes of $Hg^{II}_{gaseous}$ and $Hg^{II}_{particulate}$ in Asia and North America are 10.7 and 6.1 μg m^{-2} yr^{-1}, respectively. The total deposition flux globally to terrestrial surfaces and oceans are estimated at ~3000 and ~4000 Mg yr^{-1}, respectively, and are relatively consistent between different studies (Amos et al., 2013; Driscoll et al., 2013; Zhu et al., 2016).

A current challenge, however, is that various dry deposition measurements and modeling schemes have uncertainty factors greater than two (Wright et al. 2016). Dry deposition flux measurements of atmospheric Hg can be broadly divided into three categories: micrometeorological methods based on gradient measurements, dynamic gas flux chambers, and surrogate surface passive samplers, that have been more widely used in recent years (Lyman et al. 2009, Zhang et al. 2009, Lyman et al. 2010a, Gustin et al. 2011, Pirrone et al. 2013, Gustin et al. 2015, Huang and Gustin 2015). For modeling of deposition, resistance approaches are widely used in local and global chemical transport models applying dry deposition velocities for Hg^{II} and measured or estimated Hg^{II} concentrations (Lin et al. 2006, Zhang et al.

2009). For simulations of net Hg^0 deposition, bidirectional soil–vegetation–air exchange models are needed (Bash et al. 2007, Zhang et al. 2009) but are currently not well constrained. Models have been used to estimate total mercury deposition, in comparison with existing measurements, and to attribute deposition to sources in the context of policy (UNEP/AMAP 2015). Different models show consistent global mercury deposition patterns, especially near source regions, and can reproduce major features of observed wet deposition (Travnikov et al. 2017). However, in some regions, there are substantial differences in simulated attribution of deposition to local vs. international sources (UNEP/AMAP 2015).

Recent studies demonstrate that litterfall deposition (uptake of Hg^0 by plant foliage and transfer to ecosystems after senescence) is the predominant source of Hg to terrestrial ecosystems globally, estimated at 1,020–1,230 Mg (Obrist 2007, Risch et al. 2012a, Fu et al. 2016a, Fu et al. 2016b, Wang et al. 2016, Wright et al. 2016, Zhang et al. 2016c). In addition, throughfall deposition may contribute approximately an additional 50% of litterfall deposition (Wang et al. 2016), which would result in a global deposition of Hg in the range of 560 Mg yr^{-1}, although this magnitude needs further observational confirmation. Plant contributions (litterfall plus throughfall – wet deposition) dominate deposition loads in forests globally (btw. 70 to 85%) of which the large majority (e.g., 75%; with the exception of South American rainforests) is litterfall (Wang et al. 2016). Wright et al. (2016) and Wang et al. (2016) show large continental differences with unusually high litterfall fluxes in the Amazon and China exceeding fluxes in North America and Europe more than five times, and suggest that deposition flux decreases spatially from tropical to temperate/boreal regions with 30% of total deposition in the temperate and boreal regions and 70% of total deposition in the tropical/subtropical regions. Unfortunately, there is an almost complete lack of plant Hg data and associated Hg litterfall and throughfall deposition outside of forest ecosystems, so that estimates for global grassland, savannas, and shrublands currently remain highly uncertain.

B. Terrestrial Hg Cycling

Sources: Increasing evidence shows that the dominant Hg source in terrestrial ecosystems (vegetation and surface soils) is atmospheric Hg^0 uptake and deposition through plant litterfall that often exceeds direct wet deposition (Iverfeldt 1991, Munthe et al. 1995, Grigal et al. 2000, St. Louis et al. 2001, Grigal 2003). Using Hg stable isotope approaches, it has been demonstrated that Hg^0 deposited by plants comprises the majority of Hg deposition to soils in central North America (57–94%) (Demers et al. 2013, Zheng et al. 2016), Alaskan tundra soils (71%) (Obrist et al. 2017), central European peat soils (79%) (Enrico et al. 2016), boreal forest soils in North Sweden (90%) (Jiskra et al. 2015), and high mountain soils in Tibet (Wang et al. 2017). This is likely also true for other areas of the world, for example the Tropics where some of the highest litterfall Hg deposition is observed (Wang et al. 2016). Hg stable isotopes are useful to quantify such plant contributions: even-MIF anomalies (i.e., $\Delta^{200}Hg$) are used as a conservative tracer of atmospheric Hg^0 and Hg^{II} (Enrico et al. 2016), while small differences in odd-mass Hg isotopes ($\Delta^{199}Hg$) among foliage and atmospheric Hg^0 are attributed to volatilization of photoreduced foliar Hg (Demers et al. 2013, Enrico et al. 2016, Yu et al. 2016, Zheng et al. 2016) (Figure 2). Hg stable isotope studies estimate even higher Hg^0 contributions (up to 90%) in forest floors and soils compared to deposition studies that measure litterfall deposition. This discrepancy may be attributed to possible higher re-emission of deposition derived from Hg^{II} versus foliar Hg^0 uptake, or to the notion that litterfall measurements lack contributions from woody tissues that can account for a large fraction of above-ground forest Hg pools (50–65% and up to 200% of foliar mass (Obrist 2007, Melendez-Perez et al. 2014, Yang et al. 2014, Richardson and Friedland 2015)). Recent field studies also show evidence for an active Hg^0 sink in soils (Sigler and Lee 2006, Moore and Castro 2012, Obrist et al. 2014, Obrist et al. 2017) and possibly direct deposition of Hg^0 to forest litter (Zheng et al. 2016). The finding of the dominant terrestrial Hg^0 source fundamentally reshapes our understanding of Hg deposition to terrestrial landscapes and Hg mobility, demonstrating the need for a monitoring strategy to measure net ecosystem Hg^0 deposition, including direct exchange/deposition measurements instead of reliance on proxy methods such as leaf litterfall measurements. The dominant role of foliar Hg^0 uptake results in a specific "terrestrial" Hg isotope signature that can be used to trace terrestrial contributions and transfer to aquatic ecosystems (Tsui et al. 2012, Kwon et al. 2015), aquatic biota (Li et al. 2016), as well as lake and ocean sediments (Lepak et al. 2015, Enrico et al. 2016, Grasby et al. 2016, Araujo et al. 2017, Gleason et al. 2017).

Landscape gradients: New spatial soil data sets at regional and continental scales demonstrate that landscape Hg distribution is correlated to soil organic matter, latitude, annual precipitation, leaf area index, and vegetation greenness (Obrist et al. 2011, Richardson et al. 2013, Navrátil et al. 2014, Navrátil et al. 2016, Obrist et al. 2016). Obrist et al. (2016) explained soil Hg variability across 1911 sites in the western U.S, based on Smith et al. (2014) data, largely by Hg^0 deposition by plants which leads to high soil Hg accumulation in productive forests and soil concentrations that are 2.5 times higher than those in unproductive deserts and scrublands. Soil Hg accumulation and retention, however, also are co-determined by soil morphology and genesis as well as soil properties including soil organic matter stability, content, texture, and pH (Obrist et al. 2011, Richardson and Friedland 2015, Navrátil et al. 2016). Similar landscape gradients, with highest inorganic Hg concentrations in forested watersheds, also have been reported in river and lake sediments (Fleck et al. 2016), highlighting strong connectivity between upland Hg deposition and aquatic loadings. This is consistent with earlier studies that linked high biological Hg hotspots in the eastern U.S. to watersheds with high forest densities (Driscoll et al. 2007).

Elevation gradients, in large part associated with shifts in vegetation type, also have been observed, with vegetation and organic soil Hg concentrations and pools increasing by up to four-fold with increasing elevation (Zhang et al. 2013, Townsend et al. 2014, Blackwell and Driscoll 2015a, Wang et al. 2017). Blackwell and Driscoll (2015a) report a shift from litterfall-dominated deposition at low-elevation hardwoods to throughfall-dominated deposition in mid-elevation spruce/fir forests and cloudwater-dominated deposition in high elevation alpine forests. They also noted that cloudwater accounted for up to 71% of total deposition at the highest altitude. Hg stable isotope studies have reported both higher contributions of Hg^{II} at high elevation sites (Zheng et al. 2016), as well as lower contributions of Hg^{II} with increasing altitude (Wang et al. 2017).

Whole-ecosystem Hg^0 sink and source measurements: Few studies of Hg^0 exchange at the ecosystem level provide time-extended data to directly confirm the dominant role of Hg^0 deposition to terrestrial ecosystems. Using micrometeorological methods, the longest and most recent data set spans two years in the Arctic tundra (Obrist et al. 2017) and shows that Hg^0 deposition (6.5 ± 0.7 µg m^{-2} yr^{-1}) dominates other deposition processes (i.e., 71% of total deposition). The study also provided independent Hg stable isotope analysis that supported dominance of Hg^0 deposition. Previous year-long studies over grasslands reported annual net dry Hg^0 deposition of 17.5 µg m^{-2} yr^{-1} (Fritsche et al. 2008a) and 3.3 µg m^{-2} hr^{-1} (Castro and Moore 2016), that together with shorter-term records providing evidence of Hg^0 uptake during vegetation periods (Lee et al. 2000, Bash and Miller 2008, Fritsche et al. 2008b, Bash and Miller 2009, Sommar et al. 2016), support a terrestrial Hg^0 sink induced by vegetation. Other studies, however, are inconsistent with this notion, reporting at times large terrestrial Hg^0 emissions in the presence of vegetation (Lindberg et al. 1998, Cobos et al. 2002, Obrist et al. 2005, Cobbett and Van Heyst 2007, Baya and Van Heyst 2010), although some studies include agricultural fields with early or senescent stages of crop development and others are possibly attributable to site contamination, measurements over managed and disturbed sites, or methodological differences. Long-term deployment of existing micrometeorological methods (such as gradient-based techniques) and new techniques (Pierce et al. 2014, Osterwalder et al. 2016) are needed to better constrain net ecosystem Hg^0 sink processes. Given the importance of plant Hg^0 uptake, further research should focus on the mechanisms of Hg^0 uptake by vegetation, which remain largely unknown. Currently, indication for stomatal foliar uptake dominates in the literature (Lodenius et al. 2003, Millhollen et al. 2006, Rutter et al. 2011, Laacouri et al. 2013, Blackwell and Driscoll 2015b), although there is also evidence for non-stomatal uptake (Cavallini et al. 1999, Amado Filho et al. 2002, Stamenkovic and Gustin 2009).

The following section is a box introduction:

Box 1: Use of stable isotopes to constrain Hg cycling processes

The last ten years have seen rapid development in Hg stable isotope biogeochemistry, providing a valuable tool to quantify Hg sources and study transformation processes. Incorporation of Hg stable isotopes in global models also has the potential to constrain the relative importance of specific sources and processes (Sonke 2011, Sun et al. 2016a). The seven stable isotopes of Hg (196, 198, 199, 200, 201, 202, and 204) are subject to different mass-dependent (MDF) and mass-independent (MIF) isotope fractionation mechanisms. The isotopic signature of Hg in a natural sample carries information on its initial source and the transformation processes it underwent. Here we provide a simplified three-dimensional view of Hg stable isotope systematics and focus on exemplary processes and sources that have pronounced identifiable effects on Hg isotope signatures in environmental samples. For a more comprehensive introduction to Hg isotope fractionation and a compilation of Hg isotope variation in natural samples, we refer to the reviews of Blum et al. (2014) and Blum and Johnson (2017).

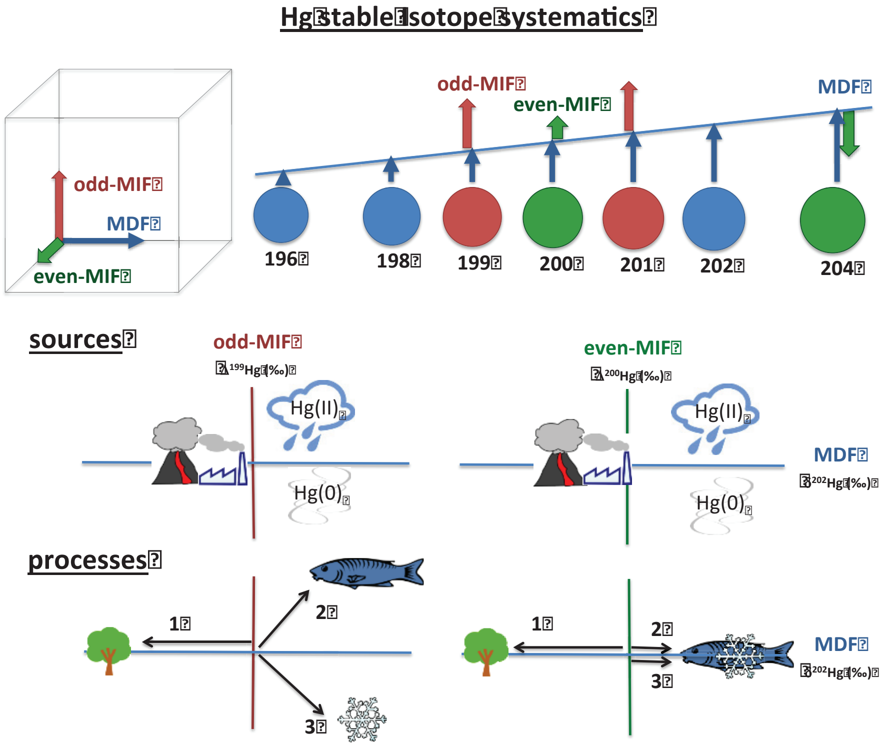

Figure 2: Simplified schematic of Hg stable isotope systematics adapted from Wiederhold et al. (2010). The seven Hg stable isotopes undergo mass dependent fractionation (MDF) proportional to their atomic mass. Anomalies from the MDF line are defined as mass-independent fractionation (MIF) of the odd-mass-number ^{199}Hg and ^{201}Hg (odd-MIF) and even-mass-number ^{200}Hg and ^{204}Hg (even-MIF) isotopes. MDF, odd-MIF, and even-MIF signatures serve as three-dimensional tracers for fingerprinting different Hg sources of natural and anthropogenic emissions, or atmospheric oxidized Hg^{II}, and elemental Hg^0 pools. Examples

of processes with large isotope fractionation factors in the environment include (1) foliar uptake of Hg^0 from the atmosphere (Demers et al. 2013, Enrico et al. 2016, Yu et al. 2016), (2) photochemical demethylation of MeHg in waters (Bergquist and Blum 2007) or (3) photochemical reduction of Hg^{II} to Hg^0 in snow (Sherman et al. 2010).

MDF (Mass dependent fractionation) is reported as $\delta^{???}$Hg in the "small delta" notation, representing the $^{202/198}$Hg ratio of a sample relative to the NIST SRM3133 international standard as defined by Blum and Bergquist (2007). Primary natural and anthropogenic Hg emission sources are generally associated with small negative $\delta^{2??}$Hg signatures, whereas atmospheric Hg pools have positive $\delta^{2??}$Hg values (Blum et al. 2014, Sun et al. 2016b). All biotic and abiotic transformation processes enrich Hg stable isotopes to different extents by MDF. One of the largest MDF fractionations observed is associated with preferential uptake of light atmospheric Hg^0 by foliage (arrow 1 in Fig. 2) (Demers et al. 2013, Enrico et al. 2016, Yu et al. 2016).

Odd-MIF (mass-independent fractionation of odd-mass-number Hg isotopes) is reported as Δ^{199}Hg and Δ^{201}Hg in the "capital delta" notation, representing the anomalies of the $^{199/198}$Hg and $^{201/198}$Hg ratios from the MDF line, respectively (Blum and Bergquist 2007). Two independent mechanisms have been experimentally shown to cause odd-MIF: (1) magnetic isotope effects (MIE) (Buchachenko 2001, Buchachenko 2009) and (2) nuclear volume fractionation (NVF) (Bigeleisen 1996, Schauble 2007). Primary Hg sources are generally associated with circum-zero odd-MIF (Sun et al. 2016b). Largest odd-MIF signatures are associated with MIE by photochemical reactions, whereas odd-MIF from NVF (identifiable by a different Δ^{199}Hg/Δ^{201}Hg ratio) is relatively small. Photochemical demethylation of MeHg to Hg^0 has been shown to cause large odd-MIF, leading to enrichment of odd-mass Hg isotopes in the residual MeHg which is preserved along the aquatic food chain (arrow 2 in Fig. 2) (Bergquist and Blum 2007). Photoreduction of Hg^{II} complexes in snow was shown to lead to large depletions of odd-mass isotopes in residual snow (arrow 3 in Fig. 2) (Sherman et al. 2010).

Even-MIF (mass-independent fractionation of even-mass-number Hg isotopes) is reported as Δ^{200}Hg and Δ^{204}Hg, representing anomalies of the $^{200/198}$Hg and $^{204/198}$Hg ratios from the MDF line (Blum and Bergquist 2007). The potential mechanisms causing even-MIF have not been identified yet, but are possibly related to oxidation of Hg^0 by halogen radicals in the atmosphere (Sun et al. 2016a). Hg^{II} in precipitation, representing atmospheric gaseous and aerosol Hg^{II}, is consistently enriched in positive anomalies of Δ^{200}Hg (and concurrent negative Δ^{204}Hg) (Gratz et al. 2010, Chen et al. 2012, Sherman et al. 2012, Demers et al. 2013, Enrico et al. 2016). The complementary pool of atmospheric Hg^0 is enriched in negative Δ^{200}Hg (and concurrent positive Δ^{204}Hg) anomalies (Gratz et al. 2010, Demers et al. 2013, Demers et al. 2015, Enrico et al. 2016, Obrist et al. 2017). Note that the possible mechanisms for even-MIF are not necessarily associated with the ^{200}Hg and ^{204}Hg isotopes only, and may also affect the $^{202/198}$Hg ratio that is used for normalisation.

End of the box section

C. Aquatic Hg cycling:

Sources of Hg to freshwater and marine environments: Recent work suggests that direct anthropogenic Hg releases to freshwaters are at minimum ~1000 Mg yr^{-1} globally (Kocman et al. 2017). In developing regions, these direct releases are generally the largest Hg source to freshwaters. Artisanal and small-scale gold mining is the largest direct Hg source globally to land and water (~880 Mg yr^{-1}), although the proportion released to aquatic ecosystems is not certain but is estimated at ~50%. This source dominates aquatic Hg inputs in South America, Africa, and Indonesia (Kocman et al. 2017). In India and China, industrial sources from the chlor-alkali industry, Hg and large-scale gold production, non-ferrous metal production, and Hg-containing waste release ~86 Mg yr^{-1} to lakes and rivers, accounting for 51% of global aquatic releases from these sources (Kocman et al. 2017). In watersheds of the Americas with historic Hg and precious metal mining, runoff from contaminated sites dominates aquatic loads and globally is substantial (44 Mg/year globally) (Kocman et al. 2017). In contrast, in developed regions including Europe and North America, catchment inputs and atmospheric deposition are generally the primary Hg sources, with background terrestrial environments accounting for ~230 Mg yr^{-1} (170–300 Mg) of riverine loads. Hydrology and DOC mobility are the major controls on delivery of catchment Hg to aquatic ecosystems, with episodic high-flow periods from storms and/or snowmelt often representing the majority of annual catchment inputs (St. Louis et al. 2016).

Recent applications of Hg stable isotope analyses have been able to differentiate among inorganic Hg sources to freshwaters. In remote Canadian lakes, lake waters share the positive Δ^{200}Hg signature observed in precipitation (Gratz et al. 2010, Chen et al. 2012, Demers et al. 2013, Rolison et al. 2013, Fu et al. 2014, Wang et al. 2015), suggesting that atmospheric deposition is the major Hg source (42 ± 26%) to these lakes (Chen et al. 2016). Similarly, analyses of sediment of the Laurentian Great Lakes indicate that atmospheric Hg^{II} deposition is the dominant Hg source to Lakes Huron, Superior, and Michigan while terrestrial catchment and industrial effluent are the dominant sources to Lakes Erie and Ontario (Jackson et al. 2015, Lepak et al. 2015). Analyses of dated lake sediment cores and catchment soils using geochemical tracers also can be used to tease apart changes in atmospheric and terrestrial Hg^{II} inputs through time (Fitzgerald et al. 2005, Perry et al. 2005, Landers et al. 2008, Muir et al. 2009, Kirk et al. 2011, Hermanns and Biester 2013). Analyses of Hg stable isotopes in dated lake sediment cores recently have been used to examine changing sources through time as well (Sonke et al. 2010, Gehrke et al. 2011, Cooke et al. 2013, Donovan et al. 2013).

For pelagic ocean regions, the dominant source of Hg is atmospheric deposition (Soerensen et al. 2010). Rivers comprise only a small fraction of input to most ocean basins because the majority is in the particle phase and settles in ocean margins. Zhang et al. (2015b) showed that the fraction of riverine Hg exported to the open ocean is 6–25% for all basins but the Arctic. In the Arctic Ocean, Fisher et al. (2012) reported river input of 80 Mg yr^{-1} which subsequently was reduced to 50 Mg yr^{-1} (Dastoor et al. 2015, Zhang et al. 2015b) but still dominant compared to atmospheric deposition of 45 Mg yr^{-1}. In the Arctic Ocean, a larger fraction of riverine Hg is exported to the central Arctic basin than elsewhere (Fisher et al. 2012, Zhang et al. 2015b). A recent study reports that the source for elevated Arctic river Hg loads is atmospheric Hg^0 uptake by tundra ecosystems (Obrist et al. 2017).

Methylmercury (MeHg) production in aquatic ecosystems: The largest source of MeHg to freshwater lakes and wetlands is *in situ* microbial production with surface sediments generally a larger producer than the water column. The activity of methylating microbes is controlled by temperature, redox conditions, pH, and the presence of suitable electron donors (e.g., organic carbon) and acceptors (e.g., sulfate, Fe^{III}, methane). The primary controls on inorganic Hg bioavailability include DOC, sulfur, and Hg^{II} concentration and speciation (Benoit et al. 1999, Boening 2000, Ullrich et al. 2001, Gilmour et al. 2013, Hsu-Kim et al. 2013). A breakthrough paper by Parks et al. (2013) identified a two-gene cluster (hgcA and hgcB) in microbes involved in Hg methylation. The hgcA gene encodes for a putative corrinoid protein capable of transferring a methyl group to Hg^{II}, and the HgcB protein returns HgcA to a redox state that enables it to receive a new methyl group. Subsequent work identified these genes in many organisms, including sulfate and iron-reducing bacteria and methanogens (Gilmour et al. 2013, Yu et al. 2013, Podar et al. 2015). Several studies have developed hgcA probes to screen aquatic sediments for Hg-methylating microorganisms (Bae et al. 2014, Schaefer et al. 2014, Bravo et al. 2015, Du et al. 2017) and to demonstrate that different methylating microbes inhabit various niches, such as regions of wetlands with varying sulfate concentrations (Bae et al. 2014, Schaefer et al. 2014). Recent development of a broad range of probes spanning all known hgcAB genes (Christensen et al. 2016) may allow future quantification of methylating potential in environmental samples.

One conundrum that remains is how to explain high levels of MeHg in marine seawater where MeHg production is still poorly understood. Gionfriddo et al. (2016) found the micro-aerophilic, nitrite-oxidizing bacterium, *Nitrospina*, in Antarctic sea ice and brine contains genes with some slight rearrangement of the hgcAB genes, suggesting that diverse microbial communities may be capable of methylation. Marine species are responsible for a large fraction of human exposure to MeHg, making an understanding of MeHg dynamics in marine environments particularly important (Gribble et al. 2016). For example, Sunderland (2007) found that for the U.S. more than 90% of MeHg exposure is from marine and estuarine species. Fitzgerald et al. (2007) suggested most marine MeHg is produced in ocean margin sediments, but since this time, a variety of studies across most major ocean basins have observed strong evidence for water column MeHg production (Cossa et al. 2009, Sunderland et al. 2009, Heimbürger et al. 2010, Cossa et al. 2011, Lehnherr et al. 2011, Blum et al. 2013). In the last several years, the abundance of ocean water concentration measurements has increased dramatically with new data from the North Pacific (Kim et al. 2017); North Atlantic (Bowman et al. 2014); Equatorial, South Atlantic, and Pacific (Munson et al. 2015, Bowman et al. 2016) oceans; Arctic (Heimbürger et al. 2015) and Antarctic Oceans (Gionfriddo et al. 2016). In the coastal marine environment, Schartup et al. (2015) used enriched Hg isotope incubations to measure active methylation for the first time in the oxic estuarine seawater. Methylation was facilitated by the presence of labile terrestrial DOC and the shift in ionic strength and microbial activity that accompanies the transition into saline waters in estuaries. Similarly, Ortiz et al. (2015) measured active methylation in laboratory experiments with marine snow aggregates.

Advances have been made in understanding the availability of MeHg for uptake to aquatic food webs (see synthesis paper 3 (Eagles-Smith et al. 2017) for details). The photochemical demethylation of MeHg has been shown experimentally to result in a large enrichment of odd-mass-numbered Hg isotopes (Δ^{199}Hg; Figure 2) in the residual MeHg pool, accumulated through the food web (Bergquist and Blum 2007). Odd-MIF anomalies in aquatic organisms were used as source tracers to distinguish between MeHg derived from sediments with low odd-MIF and open ocean MeHg with large odd-MIF (Senn et al. 2010, Blum et al. 2013). Odd-MIF anomalies in biota have been hypothesized to serve as source tracers and also as a proxy for ecological parameters such as foraging depth, with the largest odd-MIF anomalies found in fish feeding in surface waters where photochemical de-methylation is most active (Blum et al. 2013). The extent of odd-MIF in aquatic organisms has been shown to be reduced where light penetration in the aquatic water column was inhibited (e.g., by sea ice [(Point et al. 2011, Masbou et al. 2015) or DOC (Sherman and Blum 2013) and can therefore serve as a tracer for changes in climatological/environmental parameters such as sea ice cover. Field measurements and experimental data suggest that DOC controls MeHg availability for uptake in freshwaters. French et al. (2014) observed a water column DOC threshold of 8.6–8.8 mg/L, above which MeHg uptake was inhibited in Arctic lakes while Jonsson et al. (2014) showed that in estuarine microcosms, DOC-bound MeHg was 5 to 250 times more available for bioaccumulation into lower food web organisms than newly produced MeHg.

3. Anticipated impacts from human and natural perturbations, including emission changes and climate change, on global Hg cycling

A. Atmosphere

Anthropogenic emission changes impacting future global Hg cycling include Hg emission control strategies (e.g., Minamata Convention, in synthesis paper 4 (Selin et al. 2017)) and mitigation measures for global climate change. Streets et al. (2009) projected the range of 2050 global Hg emissions to be 2390–4860 Mg, compared to the 2006 level (2480 Mg). Large-scale deployment of advanced Hg sorbent technologies, such as activated carbon injection (ACI), offers the promise of lowering the 2050 emission range to 1670–3480 Mg yr^{-1}. A study by Giang et al. (2015) suggested 90 and 150 Mg yr^{-1} of avoided power sector emissions for China and India in 2050, respectively, due to Minamata Convention control technology requirements. Declining Hg emissions in China through 2050, however, could be offset by increasing Indian emissions (Giang et al. 2015), leading to a shift in source areas globally toward the Tropics. Rafaj et al. (2013) evaluated the co-benefit of global greenhouse gas mitigation efforts and found that anthropogenic Hg emissions under the global climate mitigation regime will be reduced in 2050 by 45% when compared to the case without climate measures. Pacyna et al. (2016) estimated that a best-case scenario of emission decreases by 2050 could result in a decrease of up to 50% in the Northern Hemisphere and 35% in the Southern Hemisphere.

Lei et al. (2014) compared the influence of projected emission changes and climate change on U.S. atmospheric Hg levels in 2050, finding that anthropogenic emissions contribute 32–53% of projected changes in Hg air concentration, while climate and natural emission changes account for 47–68%. Of the effects of climate change, influences via secondary emissions and ecosystem structure (section 2B) likely exert the largest changes on atmospheric Hg pools. Although likely less important, atmospheric processes also can be directly impacted by climate change, for example, as the oxidation rate constant of the Hg-Br reaction is sensitive to temperature. Zhang et al. (2016a) estimated a 5–7% increase in Northern Hemisphere atmospheric surface Hg^0 concentrations by 2050 because of reduced oxidation and increased in-cloud reduction. Changes in precipitation patterns can change in spatial distribution, magnitude, and seasonal variation of Hg^{II} deposition. Megaritis et al. (2014) projected increases in Hg^{II} deposition to the eastern U.S. from climate changes by 2050 of 6% during summer and 4% during winter, with significant spatial variability. Zhang et al. (2016a) predicted that land use and land cover changes may lead to increases in Hg^0 dry deposition fluxes under future climate. Hansen et al. (2015) projected climate-induced decreases in deposition to the Arctic, while Zhang et al. (2016a) estimated increases in northern high latitudes. Large-scale meteorological patterns such as El Niño-Southern Oscillation also can influence interannual variability of atmospheric Hg concentrations (Slemr et al. 2016).

B. Terrestrial:

Major impacts on global Hg cycling may be induced by shifts in global biomes, changes in hydrology, fire regimes, water table depth, soil moisture, and redox conditions. In addition, forestry practices and deforestation have major implications of watershed processes and methyl-Hg exposures and biomagnification, which are discussed in detail in synthesis paper 2 (Hsu-Kim et al. 2017). Based on the discussed importance of vegetation for Hg deposition, predicted shifts in biomes will directly impact terrestrial and aquatic Hg distribution and impacts. Modeling studies have predicted strong sensitivity of changes in vegetation for Hg^0 dry deposition (Krabbenhoft and Sunderland 2013, Zhang et al. 2016a). Zhang et al. (2016a) projected that by 2050 annual mean Hg^0 dry deposition flux over land would increase by 20% in northern mid-latitudes, driven by a combination of increased atmospheric Hg^0 exposure and increased vegetation and foliage density induced by CO_2 fertilization. Regionally decreased Hg^0 dry deposition, however, may occur in South Asia and Africa, for example, where projected increases of agricultural land area lead to losses of leaf areas. Strong shifts also have been suggested to occur for soil Hg accumulation. Hararuk et al. (2013) suggested that along with changes in soil organic carbon, soil Hg sequestration in the U.S. would increase by 2100, mainly induced by changes in precipitation patterns. They also predicted that increases in CO_2 concentrations to 700 ppm would stimulate both soil carbon and soil Hg accruals, while increased air temperatures would have small negative effects on both. The combined effects of increased CO_2, increased temperature, and increased or decreased precipitation regimes would lead to pronounced regional differences in changes of soil Hg stocks. Anticipated changes in forest types – in particular, coniferous versus deciduous forest abundance – likely will impact terrestrial Hg distribution as well. Comparing differences in Hg accumulation between deciduous and coniferous forests, Richardson and Friedland (2015) suggested that anticipated losses of 2.2 million ha of coniferous forests would lead to 27 Mg less Hg sequestered in organic horizons across this region, either as a function of reduced atmospheric Hg sequestration or increased leaching to watersheds. Such anticipated effects of climate change and ecosystem properties on Hg cycling can be seen clearly in archive studies. In a remote lake in Patagonia, pre-anthropogenic changes in sediment loads up to a factor of four were found, comparable to recent anthropogenic forcing (Hermanns et al. 2013), and were attributed to past changes in deposition environments induced by changes in terrestrial organic matter flux and DOM leaching from catchment soils induced by changes in climate. Similarly, Rydberg et al. (2015) documented how a climate-induced change from deciduous to coniferous forests ~5700 years BP led to reduced soil erosion and increased transport of DOC-bound Hg from a catchment in Germany resulting in increased Hg-concentrations and accumulation rates.

Clearly, other ecosystem disturbances will affect future Hg cycling, with often unknown directions and consequences. For example, responses to changes in wildfire frequency and abundance will directly impact atmospheric emissions and watershed fluxes but will not be linear given the complex relationships of emissions to fire intensities, pre-fire Hg accumulation, and post-fire mobilization – as discussed in chapter 2B. A recent modeling study (Kumar et al., in review) estimated global wildfire emission of 612 Mg yr^{-1} to increase by 14% due to climate change, yet an opposite trend (-13%) due to a decline in African driven agricultural land expansion. Yet land use changes could regionally result in emission increases as well, such as in North America (+32%) and Asia (+13%). Finally, the authors also propose that anthropogenic Hg enrichments in ecosystems could further stimulate increased wildfire emissions by 2050. Land-use changes – in particular associated with land management practices, including forestry – have large potential to mobilize terrestrial Hg pools, via increased erosion, changed hydrological pathways, and changes in yields (Kronberg et al. 2016, Kocman et al. 2017). Kocman et al. (2017) summarized studies that show pronounced soil Hg leaching when soils are converted to agricultural land and predict that global deforestation of 13 million ha yr^{-1} in the 2000s could yield up to a range of 260 Mg Hg yr^{-1} entering local freshwaters.

C. Freshwater ecosystems and oceans

Due to relatively rapid water turnover times, freshwater likely responds more rapidly to changing emissions and climate-induced changes than oceans. Modeling studies show that response times for lakes with different characteristics can range from a few years to many decades (Harris et al. 2007, Knightes et al. 2009). Recovery of freshwater ecosystems to decreased atmospheric emissions is expected when reduced atmospheric Hg loadings translate into substantial decrease in DOC-bound catchment MeHg and inorganic Hg runoff (Graham et al. 2013, Chiasson-Gould et al. 2014, French et al. 2014, Jonsson et al. 2014, Lepak et al. 2015, Ndu et al. 2015). A recent long-term mass balance study in New York state suggests a mechanism by which catchment Hg inputs to lakes with forested catchments could be very responsive to decreased emissions (Gerson and Driscoll 2016). They reported a 25% reduction in atmospheric Hg^0 concentrations resulting in a 40% reduction in litterfall Hg fluxes which in turn decreased inorganic Hg and MeHg stream inputs (45% and 29%, respectively) and lake concentrations during a 10-year period (Gerson and Driscoll 2016).

A common disturbance of river, stream, and lake Hg cycling results from widespread reservoir creation which generally amplify MeHg production; reservoir effects are discussed in detail in synthesis papers 2 and 3 (Eagles-Smith et al. 2017, Hsu-Kim et al. 2017). Most studies of climate change impacts on freshwater Hg cycling have been conducted in sensitive ecosystems experiencing accelerated changes (e.g., high altitude and latitude lakes and ponds and peatlands). In the western Canadian Arctic, where ~15% of the water bodies have shoreline retrogressive thaw slump lakes, lake sediment cores demonstrated increased sedimentation of inorganics and decreased sediment concentrations of OC, THg, and MeHg (Deison et al. 2012). In contrast, a survey of MeHg accumulation in invertebrates in tundra lakes suggests that lakes with low DOC are experiencing increased DOC input because of humification and may see a 2−3 fold increase in Hg bioaccumulation as the threshold DOC concentration of ~8 mg/L is approached (MacMillan et al. 2015). Jonsson et al. (2017) predicted a three- to six-fold increase in MeHg concentration in estuarine zooplankton in association with a projected increase in terrestrial runoff. Peat mesocosm experiments suggest changes in hydrological regimes and shift in vascular plant communities may have strong impact on Hg cycling in peatlands (Haynes 2017). For example, lowered, more variable water tables and the removal of Ericaceae shrubs significantly enhanced inorganic Hg and MeHg mobility in peat pore waters and MeHg export in snowmelt, likely from enhanced peat decomposition and internal regeneration of electron acceptors related to water table changes (Haynes et al. 2017).

Large-scale changes in the marine environment expected from climate change were explored by Krabbenhoft and Sunderland (2013). Increased seawater temperatures may enhance organic matter remineralization and the propensity for MeHg production in some regions of the ocean. Rapid changes in sea-ice cover and seasonality in the polar oceans is likely to exert a major impact on air-sea exchange of Hg in these regions. Changes in microbial community structure and ocean productivity will propagate through marine food webs in potentially unexpected ways, altering bioaccumulation. Fisher et al. (2013) used 30 years of satellite data to quantify the impacts of interannual variability in meteorology on inorganic Hg dynamics in the Arctic. They concluded that the dominant climate mode of the future in the Arctic may result in a lower reservoir of Hg in the Arctic Ocean because of enhanced air-sea exchange. This work did not consider the effects of a changing/melting terrestrial landscape, which may dramatically increase input to the Arctic from the terrestrial environment. Soerensen et al. (2016) suggested rivers are likely to become more dominant sources of Hg and MeHg in the future Arctic Ocean. Stern et al. (2012) reviewed a variety of changes that are occurring and expected to occur in the Arctic Ocean in the future, suggesting that effects are likely to be large, but also highlighted current limitations in understanding multiple, simultaneously occurring impacts on Hg cycling and bioaccumulation. Finally, recent modeling suggests the response times of marine fish tissue burdens to changes in Hg input will depend on the locations of methylmercury production (Li et al. 2016). Benthic sediment will respond much more slowly than the upper Ocean and estuarine surface waters (Sunderland et al. 2010, Schartup et al. 2015, Soerensen et al. 2016). Amos et al. (2013) showed that legacy Hg will be present in global ecosystems for periods ranging from decades to millennia, suggesting a large time lag in response to changes in inputs by anthropogenic emissions and impacts of climate change.

4. Recommendations for future research

Recommendations to improve our current understanding of processes as well as predictions of future changes in global Hg cycling include the following: (i) increased emphasis on measurement of atmospheric dry deposition, particularly Hg(0) in terrestrial environments; (ii) measurements of vertical atmospheric profiles of Hg and atmospheric processes in under-sampled regions such as the Southern Hemisphere; (iii) continued research on new methods to improve the measurements of speciated atmospheric mercury and oxidation pathways; (iv) assessment of effectiveness of post-Minamata Hg emission control measures; (v) study of critical climate change impacts on global cycling, including re-emission processes from land and water as important sources of atmospheric Hg; (vi) improved study inter-compartmental Hg exchange using measurements and models spanning various climate and ecosystem types; (vii) processes and pathways of plant Hg uptake and transfer; and (viii) study of residence times and sequestration of Hg in soils and oceans as two of the major global Hg storage reservoirs.

Challenges and Opportunities for Managing Aquatic Mercury Pollution in Altered Landscapes

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Theme 2 Synthesis for the 13th *International Conference on Mercury as a Global Pollutant*
Providence, Rhode Island
July 16-21, 2017

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Abstract

The environmental cycling of mercury (Hg) can be affected by natural and anthropogenic perturbations. Of particular concern is how these perturbations increase mobilization of Hg from sites and alter the formation and bioaccumulation of monomethylmercury (MeHg), the toxic form of Hg for humans and wildlife. The scientific community has made significant advances in recent years in understanding the processes contributing to the risk of MeHg in the environment. The objective of this paper is to synthesize the scientific understanding of how mercury cycling in the aquatic environment is influenced by natural and anthropogenic perturbations at the local scale, perturbations that include watershed loadings, deforestation, reservoir and wetland creation, rice production, urbanization, mining and industrial point source pollution, and remediation. This synthesis focuses on the major challenges imparted by each type of perturbation and management opportunities that could lead to reduction of MeHg in biota and exposure to humans. For example, our understanding of approximate response times to changes of Hg loadings from various sources or landscape alterations could lead to policies that prioritize reductions of certain activities in the most vulnerable systems and sequestration of Hg in deep soil and sediment pools. The remediation of Hg pollution from historical mining and other industries is shifting towards *in situ* technologies that could be less disruptive and less costly than conventional approaches. Likewise, contemporary artisanal gold mining has well-documented impacts with respect to Hg; however, significant social and political challenges remain in implanting effective policies to minimize Hg use. Much remains to be learned as we

strive towards meaningful application of our understanding for stakeholders, including communities living near Hg-polluted sites, decision makers of environmental policies, and scientists and engineers tasked with developing watershed management solutions. Site-specific assessments of MeHg risk will require methods to predict the impacts of anthropogenic perturbations and an understanding of the complexity of Hg cycling at the local scale.

1. Introduction

Global efforts sparked by the Minamata Convention are underway to reduce releases of mercury (Hg) to the environment (Selin et al. 2017). These efforts in addition to global perturbations such as climate change have the potential to greatly alter the worldwide distribution and impact of Hg, as described in companion Hg synthesis papers (Eagles-Smith et al. 2017, Obrist et al. 2017, Selin et al. 2017). Mercury risk can also be ameliorated by strategic management of individual ecosystems. In this synthesis paper we review and evaluate the many site-specific human activities that can affect Hg transport, methylation, and bioaccumulation, including anthropogenic alterations to landscapes such as mining and forestry operations, urbanization, rice cultivation, nutrient loadings, wetland and reservoir creation and management, as well as industrial contamination.

While environmental releases of Hg are typically in an inorganic form, concerns about human and wildlife exposure are mostly related to monomethylmercury (MeHg) accumulated in fish and other food. MeHg is produced in ecosystems through naturally occurring processes that convert inorganic Hg to MeHg. This process and the extent of MeHg bioaccumulation are key aspects of the Hg cycle and depend on a number of conditions at the site. To illustrate the critical role of ecosystem processes in Hg risk, Figure 1 shows the broad range of MeHg levels found in the sediments and soils of over 200 perturbed systems, spanning a wide range of Hg contamination. MeHg content as a fraction of total mercury spans 3 to 4 orders of magnitude at any given total Hg content.

To evaluate the impacts of natural and anthropogenic perturbations on Hg risk, we must consider the complex array of atmospheric, hydrological, biological, ecological, and geochemical processes that control Hg transport and transformation to MeHg in the environment, as described in many previous reviews (Ullrich et al. 2001, Selin 2009, Liu et al. 2012b, Lucotte et al. 2012, Driscoll et al. 2013, Hsu-Kim et al. 2013) and highlighted briefly here. Atmospheric Hg is primarily in the gaseous elemental form, which has a relatively long atmospheric lifetime allowing for its widespread distribution (Schroeder and Munthe 1998). The oxidation of elemental Hg in the atmosphere is a key process that governs the spatial distribution of wet and dry deposition (Selin 2009). Deposited Hg can be highly reactive towards further transformation such as photochemical reduction (Amyot et al. 1997, Schroeder and Munthe 1998), incorporation into vegetation (Rea et al. 2002, Graydon et al. 2012), chelation to dissolved natural organic matter (NOM) (Aiken et al. 1998, Aiken et al. 2011), and sorption to particles (e.g. organic matter, minerals, microorganisms) (Gerbig et al. 2012, Liu et al. 2012c, Skyllberg 2012, Vost et al. 2012). In addition to direct atmospheric deposition, Hg loadings into waterways can originate from upland runoff, industrial and mining point sources, and resuspension and remobilization of contaminated sediment and soil (Selin 2009, Driscoll et al. 2013). Hg inputs to waterways are generally strongly chelated (e.g. Hg-NOM) or associated with particles (both particulate NOM and mineral particles) (Han and Gill 2005, Hsu-Kim and Sedlak 2005, Balogh et al. 2008, Schuster et al. 2008, Dittman et al. 2010).

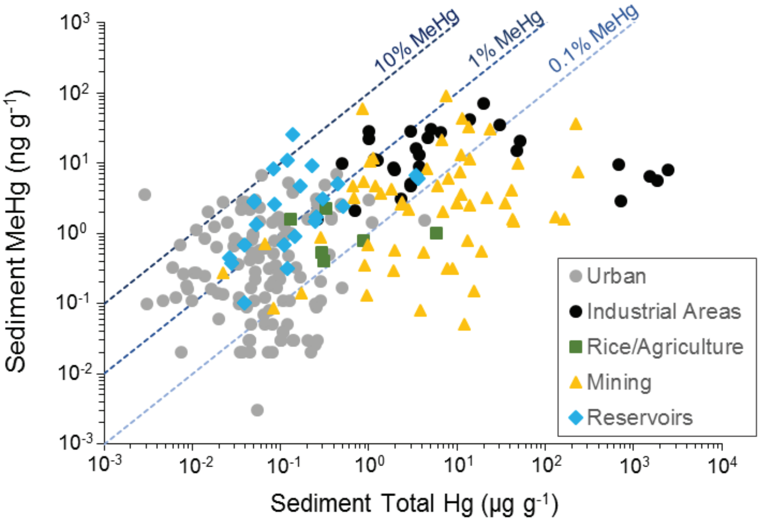

Figure 1. The cycling of Hg has been studied at a wide variety of aquatic ecosystems that have been perturbed by anthropogenic activities. Total Hg and MeHg contents at these sites span several orders of magnitude. The concerns or risks of Hg at these sites generally depend on the mobilization potential of Hg from the site as well as potential for MeHg bioaccumulation and exposure to wildlife and humans.

With the variety of Hg species and transformation processes in aquatic environments, the overall consequence is an aging effect for the metal. Recently deposited, transported or mineralized Hg tends to be more reactive towards methylation and bioaccumulation than "old" Hg that has aged in place in sediments and soil (Hintelmann et al. 2002, Paterson et al. 2006, Harris et al. 2007, Orihel et al. 2008, Jonsson et al. 2014, Jonsson et al. 2017). The aging effect for Hg may stem from the relative differences in bioavailability of weakly sorbed, amorphous or nanocrystalline Hg forms that may be more soluble at a bacterial cell interface compared to more recalcitrant forms of Hg (e.g. strongly sorbed to particulate matter, sparingly soluble microcrystalline Hg mineral phases) (Figure 2) (Deonarine and Hsu-Kim 2009, Graham et al. 2012, Jonsson et al. 2012, Zhang et al. 2012b, Pham et al. 2014). This knowledge could potentially allow site managers to develop strategies that distinguish risks between multiple sources of Hg. However, we still lack tools that can quantitatively apportion the sources of Hg towards methylation and food web accumulation potential. This is due to the complexity of the Hg biogeochemical cycle in aquatic ecosystems.

For example, Hg mobilization potential greatly depends on the biogeochemical conditions of the aquatic system. Transport of Hg in surface waters is often linked to transport of particulate and dissolved NOM (Alpers et al. 2014, Oswald et al. 2014). Thus, factors that influence NOM and particle mobilization are critical drivers of Hg transport.

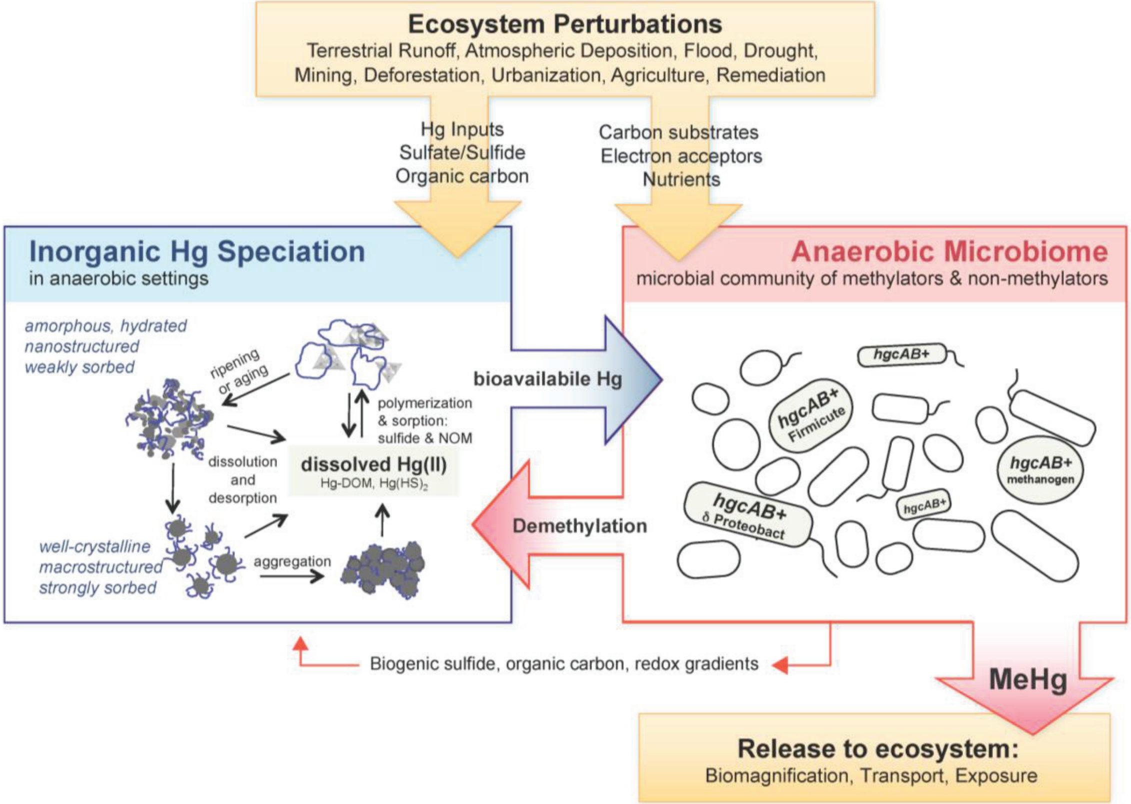

Figure 2. Perturbations to ecosystems can influence the key factors that contribute to the production of MeHg in the aquatic environment. These factors include the geochemical speciation (bioavailability) of inorganic Hg, the productivity of methylating microorganisms, and the degradation of MeHg. In most anaerobic environments, inorganic Hg is predominantly associated with particles comprising sulfides and natural organic matter (NOM). The relative bioavailability of particulate Hg can vary greatly between 'newer' forms (e.g., weakly sorbed, amorphous or nanostructured species) compared to 'older' aging states (e.g., strongly sorbed, well-crystalline, macrostructured). Hg methylation rates also depend on the growth and productivity of *hgcAB+* microorganisms, which entail a wide diversity of species that can be roughly grouped into three major clades: δ-proteobateria, firmicutes and methanogens.

The conversion of inorganic Hg to MeHg in the environment is for the most part a biological process by microorganisms that are commonly present in anaerobic sediments, saturated soils, anoxic bottom waters, as well as anoxic engineered systems (e.g., wastewater treatment, bioreactors) (Barkay and Wagner-Dobler 2005). There is also evidence of MeHg production in O_2-containing surface oceans (Lehnherr et al. 2011, Lamborg et al. 2014, Gionfriddo et al. 2016), although the mechanisms of this process are not well understood. Mercury methylating microorganisms identified to date include sulfate reducers, iron reducers, methanogens, and a handful of fermentative and syntrophic Firmicutes (Compeau and Bartha 1985, Fleming et al. 2006, Kerin et al. 2006, Ranchou-Peyruse et al. 2009, Gilmour et al. 2013a, Yu et al. 2013, Podar et al. 2015). The diversity of these organisms is still being realized; however, they all share the two gene cluster *hgcA* and *hgcB* that encode for proteins involved in intracellular methylation of inorganic Hg(II) (Parks et al. 2013). Methylating organisms are prevalent in benthic aquatic settings (e.g. saturated soil and sediment (Gilmour et al. 1992, Branfireun et al. 1999, King et al. 2000, King et al. 2002, Hines et al. 2006, Monperrus et al. 2007, Mitchell and Gilmour 2008, Avramescu et al. 2011)) as well other microenvironments with steep redox gradients (e.g., periphyton, biofilms, microbial flocs) (Mauro et al. 2001, Achá et al. 2011, Yu et al. 2013, Hamelin et al. 2015, Ortiz et al. 2015, Podar et al. 2015, Gascón Díez et al. 2016, Olsen et al. 2016).

MeHg can also be degraded by biotic and abiotic processes. These include photochemical decomposition pathways (Sellers et al. 1996, Hammerschmidt and Fitzgerald 2006, Lehnherr and St. Louis 2009, Hammerschmidt and Fitzgerald 2010, Zhang and Hsu-Kim 2010, Black et al. 2012) as well as the microbial Hg detoxification pathway encoded by the *mer* operon that can both demethylate MeHg and reduce inorganic Hg(II) to Hg^0 (Barkay and Wagner-Dobler 2005). The *mer* system is found mainly in aerobic bacteria and is believed to be inducible with sufficient Hg exposure to the organism. MeHg degradation in anaerobic niches can be rapid (Cesario 2017; Hines 2012; Tjerngren 2012), but much less is known about microbial MeHg decomposition and dark abiotic methylation processes (e.g. via sulfides) in anaerobic settings (Craig and Moreton 1984, Oremland et al. 1991, Wallschlager et al. 1995, Jonsson et al. 2016).

While net production of MeHg in aquatic systems is an important step in understanding the potential risk of mercury pollution, the biomagnification of MeHg in the food web is the driver of exposure to humans and wildlife. The process of MeHg bioaccumulation depends on many ecological factors such that food web dynamics could be the primary driver (rather than microbial methylation of Hg in benthic environments) of MeHg levels in fish and other wildlife (Eagles-Smith et al. 2017).

Overall, many factors influence Hg mobilization, transformation, and food web accumulation. While this complexity can be daunting for environmental managers and regulators, it also has the benefit of allowing for multiple avenues to be pursued that could reduce MeHg in biota. In the following text, we consider a variety of ecosystem-scale stresses and perturbations, their effects on Hg cycling in aquatic systems, and possible opportunities in policy and research to mitigate negative consequences.

2. Altered Surface Loadings

Controls on global atmospheric Hg emissions and subsequent reduction of Hg loadings to surface waters are expected to result in an eventual decrease of Hg bioaccumulation in fisheries. The timing of this response, however, has substantial uncertainty due to the legacy of stored Hg in terrestrial and sediment compartments of watersheds and the variability in Hg retention times between watersheds (Munthe et al. 2007). For example, Hg directly deposited to surface waters from the atmosphere has been observed to methylate and bioaccumulate in aquatic food webs relatively quickly (e.g. within months to 1 year), while Hg deposited to upland terrain generally requires much more time (decade or more) for subsequent impact on pelagic food webs (Harris et al. 2007, Oswald et al. 2014). Because of this time difference, the response of water bodies to an increase or decrease in Hg loadings is expected to vary widely, depending on the relative contributions of atmospheric and terrestrial Hg inputs (Table 1). Lakes and estuaries tend to have greater terrestrial Hg inputs relative to atmospheric Hg inputs, although this ratio depends on surface water area relative to watershed drainage area, the type of land cover within the drainage area (e.g. forested, urban, etc.), and the presence of known historical point sources of Hg.

While upland soils in watersheds are known to be long-term sources of total inorganic Hg to downstream surface waters, they can also be major sources of MeHg due to methylation of Hg and storage of MeHg in saturated soils (e.g., forest and wetland areas) (St. Louis et al. 1994, Mitchell et al. 2008a, 2009, Chen et al. 2012a). Land use changes that impact flow paths, including forestry practices as described below, can exacerbate MeHg flux from watersheds (e.g. (Shanley et al. 2008, Flanders et al. 2010, Babiarz et al. 2012). Terrestrially-derived MeHg may be more bioaccumulative for pelagic organisms compared to MeHg species originating from sediments (Jonsson et al. 2014). Terrestrial runoff can also shift the structure of food webs to change MeHg bioavailability and bioaccumulation pathways (Jonsson et al. 2017).

Table 1. Ratio of estimated Hg mass inputs from terrestrial sources (e.g. from river, runoff, groundwater intrusion) relative to direct atmospheric deposition to surface water for a variety of aquatic systems. Ecosystems with large terrestrial Hg:atmospheric Hg input ratios are expected to respond more slowly to anticipated reductions in global Hg emissions relative to ecosystems with low ratios that are expected to respond more quickly. Modified from (Jonsson 2013).

System	Hg Input ratio: Terrestrial/ Atmospheric	Reference
Ocean		
Global ocean (preindustrial)	0.030	(Mason and Sheu 2002)
Global ocean (current)	0.065, 0.10	(Mason and Sheu 2002), (Amos et al. 2013)
Baltic Sea	0.53	(Soerensen et al. 2016a)
Mediterranean Sea	0.70	(Rajar et al. 2007)
Arctic Ocean	2.7	(Soerensen et al. 2016a)
Estuaries		
Global Estuaries	1	(Rolfhus and Fitzgerald 1995)
San Francisco Bay (USA)	1.5	(MacLeod et al. 2005)
Tokyo Bay (Japan)	1.9	(Sakata et al. 2006)
Long Island Sound (USA)	7.9	(Balcom et al. 2004)
NY/NJ Harbor Estuary (USA)	80	(Balcom et al. 2008)
Chesapeake Bay (USA)	1.6	(Mason et al. 1999)
Lakes and Reservoirs		
Lake Superior (N. America)	0.63	(Qureshi et al. 2009)
Lake Michigan (USA)	0.31	(Qureshi et al. 2009)
Little Rock Lake (USA)	0.06	(Watras et al. 1996, Qureshi et al. 2009)
Lake Champlain (N. America)	1.6	(Gao et al. 2006)
Big Dam West (Canada)	11	(Ethier et al. 2008)
Spring Lake (USA)	0.088	(Hines and Brezonik 2007)
Lake Melville (Canada)	13	(Schartup et al. 2015)
Dongfeng Reservoir (China)	68	(Feng et al. 2009b)
Wujiangdu Reservoir (China)	27	(Feng et al. 2009b)
Petit-Saut Reservoir (French Guiana)	17	(Muresan et al. 2007)
Onondaga Lake (USA) (historical industry point source)	310	(Qureshi et al. 2009)
Clear Lake (USA) (historical mining point source)	67 – 586	(Suchanek et al. 2009)

The loading rates of other key constituents (e.g., organic carbon, sulfur, nitrogen, phosphorous) could also alter the biogeochemical cycle of Hg in local ecosystems. For example, organic carbon loadings to aquatic ecosystems can impact Hg cycling in a variety of ways. Dissolved and particulate organic matter tends to be the vehicle of Hg transport in surface waters. Thus, increased organic carbon loads often results in increased Hg loads (Schuster et al. 2008, Brigham et al. 2009, Scudder 2009, Schuster et al. 2011). Release or production of organic carbon may also coincide with the development of redox gradients in surface waters (e.g. eutrophication and stratification in lakes and reservoirs) that increase production of MeHg and bioaccumulation in hydrologically-connected zones of surface waters (e.g. anoxic hypolimnia, surface sediments) (Driscoll et al. 1995, Slotton et al. 1995, Watras et al. 1995, Herrin et al. 1998, Eckley and Hintelmann 2006, Merritt and Amirbahman 2008). Chelation of inorganic Hg(II) by NOM has the potential to lower the bioavailability of Hg for methylation. However, this effect might be masked by stimulation of Hg methylators, depending on the type of NOM (Drott et al. 2007, Kim et al. 2011, Gascón Díez et al. 2016, Mazrui et al. 2016, Bravo et al. 2017) and the limiting factor for net Hg methylation (e.g., Hg speciation, productivity of methylators, or demethylation processes) (Jonsson et al. 2012, Zhang et al. 2014b, Kucharzyk et al. 2015, Liem-Nguyen et al. 2016). Organic matter loads will also influence the structure of pelagic food webs that can result in secondary impacts on MeHg biomagnification (Jonsson et al. 2017). All of these processes demonstrate how organic carbon cycling in watershed is intertwined with Hg cycling in complex and non-linear relationships.

The impact of sulfate loadings on Hg cycling is well documented: Sulfate originating from atmospheric deposition, upland runoff, and industrial sources can stimulate the activity of sulfate-reducing bacteria in peatlands and freshwater ecosystems, resulting in enhanced production rates of MeHg (Gilmour et al. 1992, Branfireun et al. 1999, Jeremiason et al. 2006, Mitchell et al. 2008b, Wasik et al. 2012, Akerblom et al. 2013). Thus, reductions in sulfurous acid deposition has the potential to also reduce MeHg production and bioaccumulation (Hrabik and Watras 2002, Watras and Morrison 2008, Coleman Wasik et al. 2012). While this impact is straightforward, a secondary effect of sulfate is enhanced microbial production of sulfide. Inorganic sulfide will in turn alter the distribution of dissolved and particulate Hg in benthic settings (Figure 2), depending on the relative amounts of Hg, sulfide, and organic matter in the system. Models that can successfully discern the speciation of Hg (or even the bioavailable fraction) in environmental samples remain a major need for the Hg research, management and policy community.

Increased loadings of nutrients (nitrogen and phosphorous) to lakes and coastal systems and subsequent eutrophication can alter Hg biogeochemistry in numerous ways. For example, eutrophication can lower the concentrations of MeHg in biota via biodilution (i.e., lower concentrations of MeHg in primary producers and consumers due to increased biomass) (Pickhardt et al. 2002, Chen and Folt 2005, Pickhardt et al. 2005, Kim et al. 2008, Luengen and Flegal 2009, Gosnell et al. 2017). In addition to biodilution effects, eutrophication can also alter organic carbon loads to surface waters, resulting in mixed effects that can increase or decrease

MeHg levels in surface waters, as noted above. Managed alterations such as nitrate additions or hypolimnetic aeration in the field have been attempted with some success to change redox conditions and decrease MeHg concentrations in water, but these manipulations do not always result in reductions of MeHg in biota (Matthews et al. 2013, Austin et al. 2016, Beutel et al. 2016, McCord et al. 2016).

Due to the complex nature of the biogeochemical cycle of Hg, predicting the net effect of altered loadings of Hg, MeHg, organic carbon, nutrients, sulfate, and other constituents on MeHg accumulation in organisms remains a significant challenge. In this respect, management solutions that utilize a watershed loadings approach (such as total maximum daily loads in the U.S.) are difficult to formulate and to assess their efficacy. While much remains to be learned, conceptual models could still be useful for understand the main effects of altered surface loadings. For example, the predictions on the impacts of eutrophication have been successful in some cases (e.g., wastewater nutrient inputs) but not others (estuarine nutrient export to coastal waters) (Driscoll et al. 2012). Regardless, these models highlight major effects such as biodilution, increased sedimentation of Hg, and the potential for increased *in situ* production of MeHg as major impacts of eutrophication and their relative importance varies between surface water ecosystems (Driscoll et al. 2012, Soerensen et al. 2016b). Likewise, identification of the chemical forms (or aging states) of Hg and MeHg that enter surface waters can help guide policies that prioritize reductions of certain sources, or perhaps assign value terms to individual sources as a basis for economic incentives or trading programs for discharge permits. These management approaches will require a richer understanding of uncertainties associated with the assignment of values, and in particular, methods to quantify Hg and MeHg bioavailability to relevant organisms.

3. Forestry and Deforestation

Undisturbed forested ecosystems can effectively sequester atmospherically deposited Hg via accumulation in vegetation and soils (Obrist et al. 2011). This results in relatively low runoff fluxes, which are on average 6 ± 2% of atmospheric Hg deposition (Mason et al. 1997, Balogh et al. 2008, Shanley et al. 2008, Domagalski et al. 2016). Forest harvesting has been shown to impact Hg cycling as well as impact downstream ecosystems (Bishop et al. 2009, Eklof et al. 2016). An increase in total Hg and MeHg concentrations in streams and rivers draining harvested catchments have been observed in many studies (but not all studies) and have been attributed to increased soil erosion, Hg methylation activity, and/or mobilization of nearer surface Hg pools in soils (Roulet et al. 1999, Fostier et al. 2000, Roulet et al. 2000, Porvari et al. 2003, Mainville et al. 2006, Allan 2009, Sorensen et al. 2009, Lacerda et al. 2012, Eklof et al. 2013, de Wit et al. 2014, Eklof et al. 2014, Kronberg et al. 2016a, Ukonmaanaho et al. 2016). In addition to erosion, the burning of forest slash following logging (as often occurs in tropical regions where forests are converted to agriculture) has been shown to increase Hg desorption and mobility by inundating the otherwise poor soils with cations (Farella et al. 2006, Beliveau et al. 2009, Comte et al. 2013).

Regardless of the impact of forestry operations on Hg concentrations, the fluxes of Hg from harvested catchments are typically 2 times higher than undisturbed forests due to the increase in stream discharge that often occurs after logging (Porvari et al. 2003, Allan 2009, Sorensen et al. 2009, de Wit et al. 2014, Eklof et al. 2014, Kronberg et al. 2016b) (Figure 3). Discharge stems from a reduction in evapotranspiration and increased net precipitation. Forest harvesting can also increase MeHg production and/or mobilization through several mechanism. For example, decreased evapotranspiration can lead to an elevated water table, increased soil moisture, and ponding, all of which foster anoxic conditions favorable for methylaton (Munthe and Hultberg 2004, Braaten and de Wit 2016, Kronberg et al. 2016a). In addition, fresh organic carbon inputs from logging debris left on the site may enhance microbial activity and MeHg production (Eklof et al. 2016, Kronberg et al. 2016a). However, increases in catchment export of MeHg have only been observed in some studies (Porvari et al. 2003, Skyllberg et al. 2009), whereas others have shown no significant change in MeHg concentrations in response to forestry operations (Allan 2009, Eklof et al. 2013, de Wit et al. 2014, Kronberg et al. 2016a). The differing responses among studies, for MeHg as well as total Hg, are most likely due to site-specific variations in harvesting practices (e.g., the degree of soil disturbance), catchment characteristics (e.g. water table depth, slope, hydrological flow paths), and meteorological differences (timing and amount of precipitation). As such, it remains difficult to make broad generalizations about the impacts of forestry operations on Hg cycling and MeHg production.

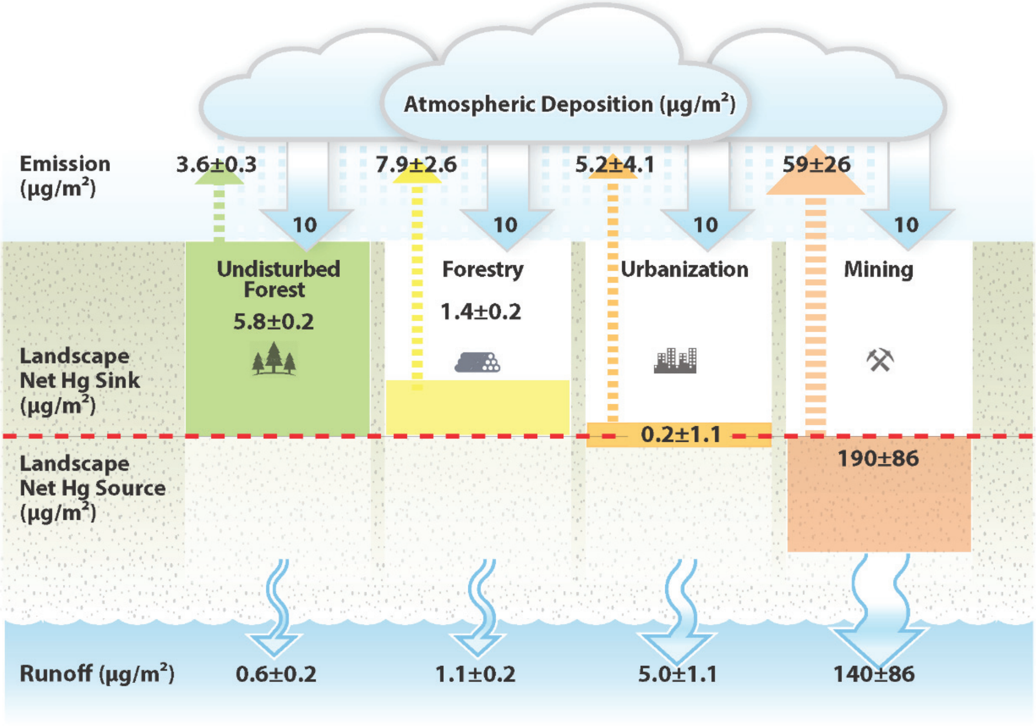

Figure 3. The influence of different landscape perturbations for Hg accumulation within catchments and Hg exports via runoff and emission. Accumulation and export loads were obtained from field studies of undisturbed forest, forested, urbanized and mine-impacted catchments and have been scaled relative to a constant atmospheric deposition (10 µg/m²).

Greater solar radiative fluxes reach the soil in harvested catchments, leading to warmer temperatures, both of which facilitate photoreduction and emission of soil-bound Hg (Mazur et al. 2014). In addition, uptake of gaseous Hg by vegetation can have a large impact on the net amount of Hg released from a landscape, and the reduction in plant uptake following forestry operations increases the net evasion of Hg to the atmosphere (Eckley et al. 2016). Surface emissions following forest harvesting may be of similar or larger magnitude to losses via aqueous fluxes (Mazur et al. 2014, Gamby et al. 2015, Eckley et al. 2016). Despite increased releases to air and water, harvested catchments are still expected to be a net-sink for atmospheric Hg inputs, albeit a less efficient one compared to undisturbed forests (Figure 3).

In addition to catchment scale impacts, several studies in boreal and temperate forests have shown that logging activity correlated with increased Hg concentrations in sediment and aquatic biota in downstream waterbodies (Garcia and Carignan 1999, 2000, Sampaio Da Silva et al. 2005, Desrosiers et al. 2006, Van Furl et al. 2010). The degree to which forestry operations contribute to the variability of Hg concentrations in fish among lakes may be relatively minor compared to other factors such as physiography and climate, and the impact is less detectable in larger lakes (Lucotte et al. 2016). An understudied area is how the potential impact of forest harvesting on other biogeochemical constituents, particularly nutrients, may alter the overall ecology of downstream aquatic ecosystems. This knowledge gap could significantly blur impacts on Hg bioaccumulation in receiving waters through processes such as growth biodilution (as noted in the previous section). Augmented NOM transport from watersheds as a function of harvesting, in addition to being a potential vector for Hg transport, may also impact photochemical transformations and thus the pools of inorganic Hg (O'Driscoll et al. 2004) and MeHg (Klapstein et al. 2017) in lake waters.

Harvesting and site preparation methods that minimize machinery damage of soils and promote rapid revegetation (e.g., winter harvesting on frozen ground) appear to result in little to no downstream MeHg impact (Sorensen et al. 2009), whereas the impacts from stump harvesting, mounding and scarification can lead to significant or highly variable impacts depending on site characteristics (Eklof et al. 2014). Other forestry best management practices, such as the protection of streamside management zones and riparian buffers, generally offer improved water quality outcomes (Lakel et al. 2010), but there is only a limited understanding of how these influence total Hg and MeHg cycling. Other common management practices, such as well-designed, located and maintained log landings, skid trails and forest roads (Brown et al. 2015), have not been well studied in relation to the management of Hg mobility and contamination, but one could postulate that surface erosion control is a factor that can affect downstream Hg transport in nearly all instances.

4. Reservoir Creation

The impoundment of rivers and streams and the subsequent creation of reservoirs are among the most common anthropogenic manipulations of freshwater aquatic ecosystems. Reservoirs typically aim to provide flood control, water supply for irrigation and hydropower. Their impacts on Hg bioaccumulation have been closely studied in numerous locations. The total area impounded by dams may rival the total surface area of natural lakes (St. Louis et al. 2000) and continues to grow, particularly in tropical regions in the southern hemisphere (Shiklomanov and Rodda 2004, Tuomola et al. 2008). The impacts of reservoir creation on Hg cycling typically result in an increase in MeHg production and can occur as part of shorter-term impacts following the construction of the reservoir as well as ongoing impacts due to hydrological, ecological and biogeochemical changes (Figure 4).

For newly created reservoirs, the increase in MeHg production and bioaccumulation results from the decomposition of flooded terrestrial organic material, which leads to increased microbial activity and increased net MeHg production in flooded soils (Mucci et al. 1995, Porvari and Verta 1995, Kelly et al. 1997, Hall and Louis 2004, Hall et al. 2004, St. Louis et al. 2004, Hall et al. 2009). However, there are several studies from reservoirs in China where elevated fish Hg concentrations do not occur (Horvat et al. 2003, He et al. 2008, Feng et al. 2009a, Liu et al. 2012a, Li et al. 2015a), presumably due to low catchment organic matter content. Because of these observations related to freshly decaying organic vegetation, reductions in catchment organic carbon prior to flooding have been proposed as a means to mitigate the impacts prior to reservoir creation (Mailman and Bodaly 2006).

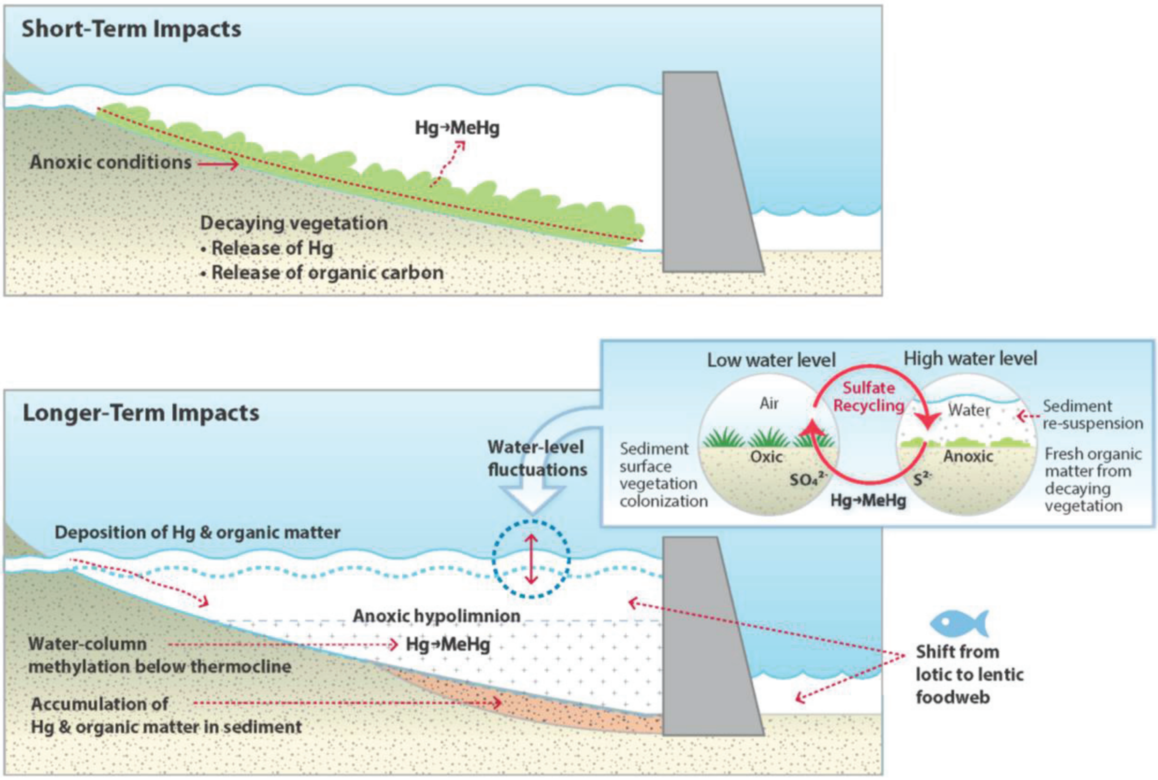

Figure 4. Conceptual diagram showing the short-term and longer-term impacts of reservoir creation on MeHg cycling and bioaccumulation. The short-term impacts of increased MeHg production are highly dependent on the organic carbon content of the flooded catchment, with some reservoir projects located in low carbon watersheds not showing an increase in MeHg.

Research over the last four decades has demonstrated that reservoirs can have elevated fish Hg concentrations compared to rivers and natural lakes (Meister et al. 1979, Montgomery et al. 2000, Brigham et al. 2002, Kamman et al. 2005); however, the extent and timing of effects varies considerably. For the well-studied boreal Canadian reservoirs, Hg in large piscivorous fish increased three- to six-fold after flooding and remained elevated above pre-impoundment levels for at least two decades (Bodaly et al. 2004, Bodaly et al. 2007, Schetagne and Therrien 2013). The extent of MeHg bioaccumulation at these sites was high enough to possibly impact fish reproduction and growth (Scheuhammer et al. 2007), although fish growth and yield may improve after reservoir formation in oligotrophic systems (Bilodeau et al. 2015). For Quebec reservoirs, peak MeHg levels occurred at 4-9 years for non-piscivorous fish and 9-11 years for piscivorous fish (Bilodeau et al. 2015). For hundreds of western US and Canadian reservoirs, the average peak in fish Hg was only 3 years after flooding, and rarely exceeded 3-times background (Willacker et al. 2016). A driver of these differences might be the lower organic carbon stores (soil and vegetation) in western catchments that were flooded relative to boreal areas.

In addition to increased MeHg production following the initial flooding, the ongoing wetting and drying cycles, as well as reservoir drawdown, can continue to affect MeHg production in older reservoirs (Orem et al. 2011, Eckley et al. 2015b). During dry periods, reduced sulfur and organic matter stored in anaerobic soils can oxidize, fueling a pulse of MeHg production on each rewetting cycle. Additionally, sulfide production during wet periods modifies dissolved NOM with reduced sulfur moieties that enhance Hg availability for methylation (Graham et al. 2012, Poulin et al. 2017). Sediment wetting and drying cycles can increase the breakdown of organic matter which can result in the increased partitioning of soil bound-Hg into the porewater phase as well as DOC production, both of which have been shown to enhance Hg methylation in reservoirs (Eckley et al. 2015a, Eckley et al. 2017). Finally, reservoir water-level fluctuations have also been shown to increase sediment erosion and re-suspension of Hg in the water column, which may make it more available for methylation (Mucci et al. 1995).

As noted above, observations of reservoirs in China have suggested less impact (relative to North American sites) on fish Hg concentrations (Larssen 2010). In addition to the relatively low organic carbon contents, these reservoirs in China had higher flow rates, shorter food webs, and increased growth biodilution (from warm eutrophic systems) that may also contribute to lower fish Hg concentrations (Horvat et al. 2003, He et al. 2008, Feng et al. 2009a, Liu et al. 2012a, Li et al. 2015a). However, unlike the research on reservoirs from North America which predict a decrease in fish Hg concentrations as the reservoir ages, in China there could be an increase in MeHg production over time as sediment organic matter accumulates from both allochthonous and autochthonous sources (Feng et al. 2009a). Autochthonous organic matter can increase as nutrients are trapped within the reservoir and the more stagnant water conditions created by the reservoir increase the production of algal biomass.

Tools to predict the timing and magnitude of reservoir construction on MeHg accumulation in food webs can help guide resource management decisions (Calder et al. 2016). Early comparisons among Canadian and Finnish reservoirs showed that reservoir age, size, temperature and organic matter content predicted the magnitude of reservoir effect (Rudd et al. 1983, Verta et al. 1986, Bodaly et al. 1993). Simple regression models using percent of total reservoir area flooded, or the ratio of flooded area:volume can predict 75-85% of variability in fish Hg for northern Canadian reservoirs (Johnston et al. 1991, Bodaly et al. 2007) especially if the upstream flooded area is included. However, no model yet exists to reliably predict responses over a wide range of conditions.

The available data and models are heavily biased to boreal and temperate systems even though most current reservoir construction projects (and some of the largest reservoirs in the world) are in the tropics and sub-tropics. Notably, boreal Canadian reservoirs may be a worst-case scenario for organic matter decomposition after flooding, due at least in part to large carbon stores in peat (St. Louis et al. 2000). Model predictions of the impacts of reservoir creation can be complicated, even in the well-studied boreal forest region of Canada. For example, regression models of existing reservoirs suggest that the upper limit on peak increases in fish Hg within reservoirs is about 6-fold above pre-impoundment levels (Johnston et al. 1991, Bodaly et al. 2007). However, a more complex probabilistic models that included a large variety of aquatic foods, site specific bioaccumulation factors and an explicit prediction of the downstream impacts to the reservoir showed that MeHg concentration could increase up to 10-fold above pre-impoundment levels (Calder et al. 2016).

There are several management options to minimize MeHg production during reservoir construction and ongoing management. For example, locations with Hg-contaminated soils or areas receiving high loads of Hg in runoff or deposition should be avoided for new reservoir construction sites. Multiple reservoirs constructed in series may compound MeHg accumulation (Feng et al. 2009a). The harvesting of biomass before flooding and extension of fill times could reduce peak MeHg concentrations after flooding (Kelly et al. 1997, Hall and Louis 2004, Mailman et al. 2006, Willacker et al. 2016), but might extend the length of an effect. With respect to long-term management of reservoirs, strategies that minimize large fluctuations in water levels between years and avoid drawdown of water storage during spring could minimize fish Hg. However, we recognize that these practices may be difficult with increasingly unpredictable precipitation patterns.

5. Urbanization

Urban areas cover a relatively small percentage of the Earth's surface (~0.5 to 3%), but are home to over half of the world's population and often include some commercial and subsistence fishing in adjoining and downstream waterways (Murkin et al. 2003, Liu et al. 2014). Hg concentrations have been shown to be elevated in urban air (Lindberg et al. 2007, Kim et al. 2009, Wip et al. 2013, Fu et al. 2015), soil/street dust (Manta et al. 2002, Ordonez et al. 2003, Eckley and Branfireun 2008a, Liang et al. 2009, Lu et al. 2009, Chen et al. 2010, Li et al. 2010b, Fang et al. 2011, Gabriel et al. 2011, Hu et al. 2011, Chen et al. 2012b, Huang et al. 2012, Dradrach and Karczewska 2013, Coufalik et al. 2014, Rodrigues et al. 2014, Zheng et al. 2015), and waterbodies (Mason and Sullivan 1998, Rice 1999, Lawson et al. 2001, Clark and Benoit

2009, Barringer et al. 2010, Rowland et al. 2010, Tong et al. 2013, Deonarine et al. 2015, McKee and Gilbreath 2015) compared to rural/natural areas. The level of Hg contamination in different urban areas can vary by over an order of magnitude, depending on the presence of current and historical industrial activities as well as local geographic and meteorological variables. In some residential and non-industrial urban areas, total Hg concentrations have been shown to not be elevated compared to rural/natural areas (Naik and Hammerschmidt 2011, Fleck et al. 2016).

In addition to changes in the total atmospheric Hg concentrations, the proportion of atmospheric Hg that is particulate-bound in urban areas can even more enriched and can result in enhanced deposition (Fu et al. 2015). The enrichment of particulate-Hg in urban air is likely a function of the proximity to emission sources and/or reactions with other urban area pollutants, such as oxidizing agents and airborne particulate matter. The deposition and accumulation of atmospheric Hg on urban impervious surfaces (e.g. buildings, roads, parking lots) often occurs in association with a thin layer of organic film from the dry deposition of gas phase pollutants (Diamond et al. 2000, Gingrich and Diamond 2001). Hg deposited to urban surfaces is relatively labile and it is estimated that roughly half can be re-emitted back to the air and the other half mobilized in runoff (Figure 3). Due to the impervious nature of many urban surfaces, deposited Hg remains exposed to direct sunlight, resulting in photoreduction and emission of Hg in urban areas (Gabriel et al. 2006, Eckley and Branfireun 2008a). Because of the high mobility of Hg in urban environments, the mass of Hg associated with urban surfaces can be very low even though the concentrations can be high.

With the low infiltration capacity of urban impervious surfaces, runoff often occurs as overland flow, which can effectively remove Hg associated with the organic film and entrain Hg street dust particles for transport to adjoining waterbodies (Vaze and Chiew 2003, Fulkerson et al. 2007, Eckley and Branfireun 2008b, 2009). As a result, urban areas typically have much higher runoff yields (on average 50 ±17%; Figure 3) compared rural areas and this yield increases with the percentage of impervious surface cover in a catchment (Eckley et al, 2008). In forested streams, dissolved NOM plays an important role in the transport of Hg in the dissolved phase (Brigham et al. 2009, Stoken et al. 2016). However, in urban areas the dissolved organic matter content can be low, and particulate-bound Hg is especially pertinent for overall mass transport (Hurley et al. 1998, Lawson et al. 2001, Lyons et al. 2006, Eckley and Branfireun 2008b).

While total Hg can be very elevated in urban waterbodies, MeHg concentrations on street dust, sediment and water have been shown to be relatively low (Huang et al. 2012) as have MeHg concentrations in fish (Scudder 2009, Chalmers et al. 2014). In general, urbanization may decrease the potential for MeHg formation by reducing the presence of anoxic conditions, which can occur through urban storm water engineering designed to rapidly convey water away from the built environment. This reduces water stagnation and also increases peak flows and erosion in urban waterways which creates conditions less favorable to methylation than depositional environments. Higher nitrogen and lower dissolved NOM in urban streams may also contribute to the lower methylation potential in urban environments. Finally, the bioavailability for methylation of urban inorganic Hg may lower due to higher proportion of inorganic Hg bound to particles in urban systems.

Low impact development/green infrastructure are a common feature of new urban developments and are designed to reduce discharge to streams and improve water quality through particle settling. Urban BMPs often include stormwater retention ponds, constructed wetlands, bioswales, permeable pavement and green roofs. Retention ponds and other constructed wetlands have been shown to be very effective at reducing metal concentrations, including total Hg; however, they can also be a net sources of MeHg (Stamenkovic et al. 2005, Rumbold and Fink 2006, Jang et al. 2010, Strickman and Mitchell 2017b). Similar to patterns observed in reservoirs, newly constructed retention ponds and wetlands differ considerably in their initial and long-term MeHg production capabilities as a function of age and organic matter content of the impounded soils (Sinclair et al. 2012, Strickman and Mitchell 2017b). The impact of MeHg from urban constructed wetlands depends on their scale and hydrological connectivity to other waterways; however, this has not yet been explored in the literature and in most circumstances they are not likely a significant contributing source of MeHg to receiving water bodies.

6. Rice Production

While human exposure to MeHg is mostly through dietary consumption of fish, exposure through rice is another possible major route that has been realized more recently, particularly for certain communities in Asia (Rothenberg et al. 2014). Rice is a major staple agricultural crop and provides the primary source of food energy for nearly half of the global population. Consequently, rice paddies are one of the most widely distributed land uses in certain regions of the world, such as South and East Asia (FAO 2002). Rice production methods can be grouped into broad categories that include irrigated rice, rainfed rice (rainfed lowland rice and rainfed upland rice) and flood-prone rice. Irrigated rice represents approximately 55% of total area of rice cultivation and 77% of the global rice production and often employs alternate wetting and drying cycles as a means to reduce freshwater consumption without decreasing yields (FAO 2013).

Rice cultivation can foster anaerobic and organic carbon-rich habitats that promote the growth of Hg methylating microbes, resulting in conditions where MeHg can accumulate in rice crops (Meng et al. 2010, Meng et al. 2011). As a result, rice consumption has been shown to be the dominant pathway of MeHg exposure for certain communities (e.g., mining areas and certain inland areas of Southern China) (Feng et al. 2007, Zhang et al. 2010, Li et al. 2012, Li et al. 2015b). Elevated concentrations of MeHg in rice grains (up to 140 µg/kg) have been reported in Indonesia (Krisnayanti et al. 2012) and different parts of China (e.g. (Horvat et al. 2003, Qiu et al. 2008, Meng et al. 2010, Meng et al. 2011, Meng et al. 2014a, Meng et al. 2014b, Liang et al. 2015, Tang et al. 2015)). MeHg bioaccumulates in rice more readily than inorganic Hg, with bioaccumulation factors for MeHg that are 800-40,0000 times higher than those for inorganic Hg (Meng et al. 2010, Zhang et al. 2010, Meng et al. 2011, Meng et al. 2014a). MeHg exposure via rice in other global regions is also a possibility. For example, a recent study reported that 30% of commercial market rice products in Europe exceeded 10% of the provisional tolerable weekly intake calculated for toddlers or 13% of products for adults with rice based diet (Brombach et al. 2017).

Rice seeds have the highest ability to accumulate MeHg compared to the other tissues (e.g. root, stalk, and leaf), and paddy soils are the principal source of MeHg to tissues of rice plants (Meng et al. 2010, Meng et al. 2011, Strickman and Mitchell 2017a). MeHg in soil can be taken up by plant roots and then translocated to the aboveground parts (leaf and stalk). In the premature plant, the majority of MeHg is stored in the leaf and stalk; however, most of this MeHg is transferred to the seed during the ripening period. On a mass basis, the majority of MeHg is found in edible white rice. During grain processing, most of the inorganic Hg (~78%) is eliminated, but the majority of the MeHg remains in the food product (~80%) (Meng et al. 2014a). MeHg in whole rice seeds as well as the edible components exists almost exclusively as CH_3Hg^+ bonded to cysteine-like structures (Li et al. 2010a, Meng et al. 2014a), in the form of individual CH_3Hg-(L-cysteinate) complex or as part of larger proteins containing cysteine moieties. This MeHg-cysteine association behaves like a mobile nutrient and is actively transported to the endosperm during seed ripening (Meng et al. 2014a). We also note that the CH_3Hg-(L-cysteinate) complex is thought to be responsible for the transfer of MeHg across the blood-brain and placental barriers (Kerper et al. 1992, Kajiwara et al. 1996, Simmons-Willis et al. 2002, Clarkson et al. 2007).

In addition to the concern for MeHg exposure via rice consumption, rice paddies can also be a source of MeHg to downstream ecosystems. Net export of MeHg from rice fields has been estimated in some locations, although this phenomenon may vary with growing season (Bachand et al. 2014, Windham-Myers et al. 2014, Tanner et al. 2017).

Management strategies to reduce MeHg in rice must be balanced with the need to maximize crop production. Water management strategies such as intermittent flooding might suppress anaerobic Hg methylating communities relative to continuously flooded rice fields (Rothenberg et al. 2011, Peng et al. 2012, Rothenberg et al. 2014, Wang et al. 2014, Rothenberg et al. 2016). Selenium (Se)-enriched soils have been shown to reduce MeHg production in paddy soils, which may be related to the formation of Hg-Se complex in the rhizosphere (Zhang et al. 2012a, Zhang et al. 2014a, Wang et al. 2016). Thus, Se amendments have been proposed as a means to reduce the absorption and accumulation of MeHg in rice grains in areas of high Hg contamination (Zhao et al. 2014, Wang et al. 2016). However, this approach requires caution due to the known impacts of Se on wildlife. Different rice cultivars also vary considerably in MeHg concentrations in the grain, suggesting that appropriate cultivar selection could be a possible way to reduce MeHg accumulation and exposure in Hg contaminated areas (Peng et al. 2012, Rothenberg and Feng 2012, Li et al. 2013). The selection of non-rice food agricultural crops (e.g. corn, rape, tobacco, and cabbage) could be another solution, as these crops do not accumulate MeHg to the same extent as observed for rice (although inorganic Hg accumulation would still occur) (Qiu et al. 2008).

Future research on the impacts of rice production for Hg requires greater geographical diversity, including Asian countries (other than China), Africa, South America, and North America. Such data are critical in assessing potential health risks that may be associated with rice cultivation in Hg-contaminated soils. While the source, distribution, and accumulation of MeHg in rice plants as well as transport and the transformation of Hg species within paddy fields have been previously studied, the processes of Hg methylation in rice paddy and its controlling factors are not fully understood. Furthermore, uptake and translocation pathways and the detoxification of MeHg in rice plant are still unknown. As is the case in other ecosystems, newly deposited Hg may be more readily transformed to MeHg in rice paddies than older Hg (Meng et al. 2010, Meng et al. 2011). However, the mechanisms behind this phenomenon are not well understood, and in this respect the linkage between MeHg concentrations in rice and atmospheric Hg deposition requires further investigation.

7. Gold mining and other mining activities

Mercury releases associated with mining can encompass a broad range of activities, including contemporary artisanal small-scale gold mining (ASGM), historical mines, and contemporary industrialized mines. ASGM generally involves the importation of Hg from other regions for recovery of gold and other precious metals. The process can entail unmechanized gold recovery and also involve small and heavy equipment by individuals and small groups (rather than multinational corporate entities that operate industrialized mines). Historically, this same Hg amalgamation process at contemporary ASGM sites was used at larger scale gold and silver mines and the legacy of these activities (as well as the legacy of Hg mines) have ongoing environmental inputs of Hg to downstream locations.

ASGM currently spans more than 70 countries, where such activity is typically little acknowledged, not regulated, or illegal (Veiga et al. 2006, Telmer and Veiga 2009, Swenson et al. 2011, Reichelt-Brushett et al. 2017). Collectively this practice represents a major global emission source of Hg to the atmosphere, with estimates ranging from 20 – 37% of total anthrophogenic Hg emissions (Lacerda 2003, Pirrone et al. 2010, United Nations Environment Programme 2013). These estimations often rely on a mass balance approach for regional imports and exports and can have a high degree of uncertainty given the lack of reliable information (Malm 1998, Lacerda 2003, Li et al. 2009, Telmer and Veiga 2009, Li et al. 2014, Grimaldi et al. 2015) and few examples of directly quantified Hg emissions (Amouroux et al. 1999, Balzino et al. 2015). ASGM also imparts health risks for workers (Gibb and O'Leary 2014, Kristensen et al. 2014, Castilhos et al. 2015) and riparian populations downstream of mining sites (Lebel et al. 1997, Grandjean et al. 1999, Maurice-Bourgoin et al. 2000, Bastos et al. 2006, Diringer et al. 2015), as described in a companion synthesis paper (Eagles-Smith et al. 2017).

The type of ASGM techniques (such as material collection, processing, and disposal techniques) and the extent of accidental spills will govern the amount of Hg release (Telmer and Veiga 2009, Balzino et al. 2015). Increases in local soil Hg contents (Malm et al. 1995, van Straaten 2000) and soil erosion rates are common features of many ASGM areas (Swenson et al.

2011), and the combination of these two features are the key towards increased Hg transport and exposure to downstream communities. Extensive deforestation is often associated with AGSM and could contribute to soil erosion and Hg export from watersheds. However, the impact of deforestation for Hg transport (relative to inadvertent release and deposition of Hg from mining itself) requires further examination, perhaps with combinations of remote sensing data (e.g. satellite land cover) and field observations of Hg mobilization in watersheds (Swenson et al. 2011, Diringer et al. 2015, Lobo et al. 2016). In this respect, the significance of terrestrial Hg inputs relative to direct atmospheric deposition to waterbodies near ASGM (i.e. as shown in Table 1) could provide useful comparisons to other systems and insights for management.

While ASGM and related processes (e.g., deforestation, soil erosion, urbanization) are known to increase transport of Hg in watersheds, related impacts on biogeochemical transformations of Hg are also possible (Boudou et al. 2005, Alanoca et al. 2016) The chemical forms of Hg mobilized from recently deforested areas may differ from other terrestrial sources, and this difference can be relevant for Hg methylation and MeHg bioaccumulation. ASGM operations sometimes utilize cyanide in conjunction with Hg amalgamation (perhaps to reduce Hg usage) or as a replacement of Hg. Environmental releases of cyanide has been hypothesized to alter methylation of Hg in downstream receiving waters perhaps by suppressing the biological activity of methylators (Tarras-Wahlberg et al. 2001, Guimaraes et al. 2011). This hypothesis remains to be fully investigated.

Contemporary industrial mining operations are very distinct in terms of their impacts on Hg cycling compared to ASGM and historical industrial mines, most notably because they do not use Hg as part of the ore extraction process. However, these mines can increase mobilization of Hg if the orebody of interest is naturally enriched in mercury (typically gold mines as well as some copper and zinc mines). Stack emissions and water discharges at mines are another source, but these are typically regulated and can be reduced through traditional pollution control technologies. Surface-to-air emissions from the ore, tailings and waste rock piles can be significant source of emissions from mines (Eckley et al. 2011a). Because of the large surface area covered by many contemporary industrial mines, the annual surface-to-air emissions scaled over the entire mine site can be >100 kg/year (Eckley et al. 2011b). These surface emissions can be substantially reduced by capping mine waste with a thin layer of low Hg content topsoil and/or applying Hg control reagents to the mine wastes, though the latter approach still needs further evaluation under field conditions (Eckley et al. 2011b, Miller and Gustin 2013).

In addition to direct releases of Hg to the air, mine operations can also impact Hg methylation in downstream aquatic systems by providing a substantial source of sulfate to receiving waterbodies (Berndt et al. 2016, Bailey et al. 2017) and by altering the surrounding hydrology as a result of dewatering around the mine pit/tunnels during operations and subsequent re-wetting after closure (Willacker et al. 2016, Eckley et al. 2017). The drawdown and wetting cycles yields similar impacts on Hg methylation as noted for reservoirs. After the stoppage of operations at open pit mines, the resulting deep pit lakes are susceptible to stratification, very high sulfate, and low organic carbon levels that have implications for MeHg production (Meier et al. 2012, Gammons et al. 2013).

Overall, Hg releases from historical and contemporary mining activities are well documented. However, strategies to manage Hg release remain an ongoing challenge, mainly due to persistent and long term inputs to ecosystems and broad geographic distribution of the impact. For example, some of the highest fish Hg concentrations in Canada are associated with area where Hg was historically used to extract gold (Lockhart et al. 2005). Similarly, Hg pollution associated with historical Hg use for gold and Hg mines during the California gold rush during the mid-1800s continues to be a concern for downstream waterbodies (May et al. 2000, Alpers et al. 2006). For contemporary ASGM, alternatives to Hg (such as cyanide, borax) have been suggested, but they also have other challenges, particularly for subsistence miners with limited resources (Hidayati et al. 2009, Spiegel and Veiga 2010, Velásquez-López et al. 2011, Veiga et al. 2014, Cordy et al. 2015, Køster-Rasmussen et al. 2016). The agreements outlined in the Minamata Convention may also help to regulate Hg trade. However, the impact on unregulated Hg markets remains uncertain. Overall, effective management of contemporary ASGM requires a comprehensive approach that takes into consideration the environmental impacts of concurrent activities as well as socioeconomic constraints in applying management strategies.

8. Industrial Point Sources and Remediation

Historical contamination of mercury from industrial inputs represents a major challenge to address for site managers and neighboring communities who may be vulnerable to mercury exposure. In addition to sites impacted by mining, other types of industrial Hg contamination includes waste discharged from chloralkali processing facilities, pulp/paper mills, oil/gas production, chemical processing, etc. The age of the contamination at any single site is often several decades old (although newer industrial contamination still occurs in areas without close monitoring or established environmental regulations). The types of impacted sites include terrestrial sites as well as surface waters where the Hg is typically concentrated in sediments (Lindeström 2001, Bloom et al. 2004, New York State Department of Environmental Conservation and U.S. Environmental Protection Agency 2005, Tomiyasu et al. 2006, Skyllberg et al. 2007, Ullrich et al. 2007a, Ullrich et al. 2007b, Bravo et al. 2009, Bravo et al. 2014, Balogh et al. 2015). Industrially impacted sites also include subsurface zones where groundwater discharge of Hg into surface waters would be of concern (Flanders et al. 2010, Southworth et al. 2010). In many of these systems, total Hg contents in soil and sediment are enriched by orders of magnitude relative to other ecosystems where Hg is also a concern (Figure 1). In some exceptional cases, exposure of inorganic Hg from soil or vapors might pose a direct health risk (Robins et al. 2012, Hagan et al. 2013, Hagan et al. 2015). Nevertheless, most industrially-polluted sites are a concern because of MeHg bioaccumulation, mobilization of Hg to downstream locations, and/or via evasion to the atmosphere. We note that our search of published literature of industrially-contaminated sites revealed sediment MeHg contents that tended to be greater than other types of sites with comparable total Hg contents (e.g., mining sites) (Figure 1). This observation might be due to research activities prioritized towards sites with potential health risks (i.e. sites with high levels of MeHg production and bioaccumulation) relative to other industrial sites with little MeHg impact.

The management approach for industrially contaminated locations requires initial risk assessments of the mercury contamination and development of strategies for remediation or long-term management (Randall and Chattopadhyay 2013, Bigham et al. 2017). In the course of developing a management and monitoring strategy, managers must formulate a benchmark goal for addressing the problem, quantify all sources of Hg to the system, and identify areas of high exposure risk (e.g., high Hg or MeHg concentration) on the path towards a remedial action plan. These decisions require models (conceptual and/or numeric) that can be used to understand relevant processes for mercury fate, and perhaps more importantly delineate the uncertainties for risk. Industrial sites can also have multiple pollutants, in addition to mercury, that drive risks, and the best remediation and management decisions for one target pollutant could increase risks of other targets.

For soil and sediment sites impacted by industrial Hg pollution, a variety of remediation strategies have been employed (Wang et al. 2004a, Wang et al. 2012, Xu et al. 2015). The most common approaches have been *ex situ* methods such as dredging and excavation for remediation of high priority Hg hotspots (Rudd et al. 2016). However for sites of lower Hg enrichment and broad spatial extent, *in situ* methods have gained substantial interest in recent years due to the inherently less disruptive impact of these methods on the surrounding ecosystem, the potential for long term mitigation, and the reduction in costs relative to dredging and excavation (Ghosh et al. 2011, Wang et al. 2012). For example, sediment caps are used for stream bank stabilization and erosion control (generally aiming to halt or minimize mobilization of Hg-bearing particles) (Wang et al. 2004b, Johnson et al. 2010). *In situ* amendments entail chemicals or materials added directly to soil or sediments to alter the biogeochemical conditions of sites. For example, nitrate amendments and active aeration of reservoirs have successfully been used to artificially elevate the redox potential of the water column as a means to eliminate or bury the anaerobic zone that fosters MeHg producing microorganisms (Matthews et al. 2013, Beutel et al. 2014). Other amendments such as black carbon sorbents and ferric iron aim to sequester Hg in sediment/soil and reduce the solubility and bioavailability of Hg and MeHg for biological uptake (Mehrotra and Sedlak 2005, Ulrich and Sedlak 2010, Gilmour et al. 2013b, Gomez-Eyles et al. 2013). We note, however, that the impact of these processes for Hg speciation remains poorly understood. For example, the addition of activated carbon has been shown to decrease, increase or not change overall levels of MeHg in sediment microcosms (Gilmour et al. 2013b), responses that might reflect reductions of Hg bioavailbilaity for methylation, reduction of MeHg availability for demethylation, or alterations to the microbial community that are essential to these processes. Nevertheless, activated carbon amendments is a promising option in some cases for reducing MeHg bioavailability to benthic biota.

Many challenges remain in the development of effective management strategies for industrially-polluted sites. Innovative tools for source attribution and risk assessment are in great need and remain an active area of research. *In situ* remediation technologies such as chemical amendments and sediment caps provide much promise; however, the implementation of these methods are for the most part currently limited to lab scale and pilot-scale testing. Full scale implementation requires a better understanding of long term effects of *in situ* technologies as well as methods to evaluate site characteristics that inform the remediation selection process.

9. Summary of Management Opportunities and Research Needs

A wide variety of anthropogenic and natural perturbations to landscapes can yield significant impacts to Hg cycling in watersheds. These impacts would be of concern if they increase exposure risks to humans and wildlife. As such, water quality criteria for Hg tend to consist of fish-based MeHg content, rather than an aquatic or soil Hg/MeHg value. While this approach for regulation provides a direct connection towards exposure and risk, this type of criterion does not offer clear ecosystem management strategies.

As noted in the preceding sections, a specific remedial action or ecosystem perturbation requires widely variable response times (e.g., years to decades) for the biogeochemical processes leading to MeHg bioaccumulation, and understanding the time scales may be the crux of any local Hg mitigation strategy. Knowledge of the relative source loadings of Hg (e.g., surface versus terrestrial loading as shown in Table 1) could offer managers insights on the variety of Hg sources to a specific site, the relative response times for control of these sources, and ecosystem management strategies to minimize MeHg bioaccumulation.

Whole water or soil/sediment total Hg or MeHg concentration criteria might be helpful as a shorter term gauge of management effectiveness, but sediment/soil Hg criteria could be misleading in that total Hg and MeHg concentrations do not necessarily correlate with MeHg bioaccumulation. As such, criteria based on a ‘bioavailable’ fraction for total Hg, bioavailable MeHg, and net Hg methylation potential should be considered as we improve the functionality of metrics for water quality management.

Approaches for assessing the potential of Hg mobilization and net methylation at sites remain a challenge. However, there have been recent gains in scientific knowledge that could be utilized by site managers. For example, the mobilization of Hg to downstream and downgradient locations is often linked to mobilization of particles (Flanders et al. 2010). Thus, Hg loadings can be predicted by particle loadings. (We note that sites impacted by liquid elemental Hg^0 contamination is an exception, where mobilization is influenced by dissolution and corrosion rates of discrete Hg^0 phases in addition to transport of secondary mineral particles) (Southworth et al. 2010). Natural organic matter can facilitate particle transport by coating particles and reducing colloidal aggregation and deposition rates. Moreover, recent research has demonstrated that this effect varies with the quality of the NOM (e.g. molecular weight, chemical structure) (Deonarine et al. 2011, Philippe and Schaumann 2014, Louie et al. 2015, Louie et al. 2016). Optical properties of dissolved NOM such as specific UV absorbance and fluorescence signatures could enable the use of real-time sensors deployed in surface waters as proxies for dissolved and colloidal Hg transport (Dittman et al. 2009, Dittman et al. 2010, Burns et al. 2013).

New tools are also in development to enable meaningful monitoring information of Hg transformation potential and source attribution. For example, stable Hg isotope signatures are a promising tool to delineate Hg loading from multiple sources (Liu et al. 2011, Bartov et al. 2013, Deonarine et al. 2013, Sherman et al. 2015, Wiederhold et al. 2015). However, the application of Hg isotopes requires measurements of the appropriate 'endmember' samples as well as an understanding of the extent of isotopic fractionation that could occur from a variety of biogeochemical transformations processes at the site. The deconvolution of fractionation processes represents the major hurdle in applying Hg isotopes for source apportionment.

Recent advances in our understanding of microbial Hg methylation also has the potential to enable new tools to monitor and quantify net MeHg production potential at field sites and perhaps enable predictive capabilities for various remediation strategies. For example, the discovery of the *hgcAB* gene cluster for methylating microorganisms has led to new biomolecular tools to quantify their abundance, and perhaps activity of methylating microbes in nature (Gilmour et al. 2013a, Parks et al. 2013, Podar et al. 2015, Christensen et al. 2016).

Likewise, methods to quantify the reactivity of Hg and bioavailability to methylating microbes, such as chemical equilibrium models or selective extractions, have been tested over the years, but with limited success (Hsu-Kim et al. 2013). These limitations might be explained by the complexity of Hg-sulfide-NOM species in soil and sediment, which include nanostructured particulate phases of varying reactivity (e.g. dissolution potential) in anaerobic settings (as shown in Figure 2) Hg uptake into methylating microbes is likely to involve an active membrane transport process (Schaefer et al. 2011, Schaefer et al. 2014), and not simply a diffusive uptake process of neutrally-charged Hg-sulfide solutes (Benoit et al. 1999). For this reason as well as challenges in differentiating between dissolved solutes and colloidal particles in water samples, chemical equilibrium models of neutral Hg species are no longer employed by the scientific community to ascertain Hg bioavailability to methylating bacteria (Hsu-Kim et al. 2013). Instead, alternate markers to quantify Hg reactivity and bioavailability are needed, especially models or biologically-relevant measurements that can accommodate the spectrum of Hg species in soil and sediment and are consistent with the process in which methylating microbes take up Hg (Ticknor et al. 2015).

While tremendous progress has been made in understanding the process of microbial Hg methylation, much remains unknown regarding the mechanism of Hg uptake, how the rates of Hg methylation vary amongst the diverse species of methylating microbes, and if their abundance or activity can even correlate to methylation rates. The process of dark MeHg degradation in benthic zones remains a greater mystery and requires more attention in the research community, especially since remediation of contaminated sites might need to focus on strategies to enhance MeHg degradation. With the improved understanding of processes that contribute to Hg mobilization and net MeHg production, novel methods for effective and lasting remediation and monitoring technologies are within reach.

Transformational improvements to Hg site management, such as those outlined above, will require some time, yet the needs for comprehensive risk assessment tools remain urgent. Typical site assessments attempt to account for all inputs and outputs to the system, which enables an understanding of major sources and sinks. Other parameters such as the concentrations and fluxes of sulfate, DOC, filter-passing Hg and MeHg fractions, dissolved and total sulfide, redox potential, etc. could provide insights to the factors controlling rates of MeHg production, degradation and food web biomagnification. In some cases, measurements of isotope ratios of Hg, bioavailable fraction of Hg, and soil/water microbiomes might be justified as the development and applications of these tools improve with additional research. Advanced techniques of data analysis have the potential to help us discern large data sets of parameters interlinked by non-linear and poorly defined relationships.

Global scale perturbations such as climate change will also impart local scale effects such as sea level rise, melting tundra soils, and altered and extreme precipitation regimes. Impacts could include large releases of soluble organic matter, mobilization of Hg-bearing particles, and redox fluctuations and gradients, all of which can ultimately impact MeHg bioaccumulation as discussed implicitly in previous sections.

Overall, this synthesis paper has outlined the effects of major anthropogenic landscape perturbations for the distribution and bioaccumulation of Hg in ecosystems. Much of the research over recent decades has a relatively narrow geographical focus (e.g. North America, Europe, parts of Asia). However in other locations (Latin America, Africa, Asia Pacific), large populations continue to be vulnerable to the negative health consequences of MeHg exposure. Insights from the existing research can provide substantive approaches to mitigate Hg distribution and exposure in understudied regions. Regardless, research in these regions is sorely needed, particularly in tropical environments that have received much less attention in the Hg biogeochemical research field. Altogether, global and local scale perturbations to landscapes alter the transport and transformations of Hg in complex ways, and an understanding of this complexity is needed to guide international and regional efforts to manage and monitor reductions of MeHg exposure to populations.

Acknowledgements

This paper was written as part of the synthesis effort for the 13th International Conference on Mercury as a Global Pollutant, Providence, Rhode Island, July 16-21, 2017. A revision of this paper will be submitted for consideration in the journal *Ambio*.

Grant support was provided by the U.S. Department of Energy Environmental System Science Program (DE-SC0017128) and the National Institute of Environmental Health Sciences Superfund Research Program (R01ES024344).