出國報告（出國類別：國際會議）

參加「第 11 屆全球汞污染國際研討會」

服務機關：行政院環境保護署空保處

姓名職稱：周怡君特約助理環境技術師

派赴國家：英國

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報告日期：102 年 10 月 28 日

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壹、研討會簡介

全球汞污染國際研討會，從 1990 年在瑞典開辦以來，已連續舉辦 20 多年，該會議每 2~3 年舉行一次，已經是一個相當受國際矚目的研討會議，本次會議由英國舉辦（圖 1 爲本屆研討會標幟），會議地點在愛丁堡，今年參加國家多達 90 多個國家，約有 850 名代表參加，會議爲期 5 天，除有超過 400 個口頭報告外，並有海報區及廠商展覽區，研討會涵蓋內容十分豐富多元。議題包含汞排放控制技術、法規、大氣汞監測等。

2013 年正值聯合國環境總署對全球汞管制的條約生效，故本次會議特別受矚目。除慶祝正式啓動該條約外，並討論如何把條約付諸實踐。爲此，本屆研討會的主題訂爲「Science informing global policy」，以全球的觀點討論 2013 年以後將面對的問題：

- 聯合國環境總署的條約將採取什麼形式，以及如何落實條約內容
- 如何抑制目前有關汞的供應及需求
- 如何減少人類活動的汞排放
- 我們需什麼評估工具，目前的監測及模擬工具是否可協助達成目標
- 汞對健康及社會的影響及未來的變化
- 如何整治受污染場址和生態系統
- 目前及未來所面臨的問題，以及條約的協同效應
- 如何將我們對汞的關注和行動由地方提昇至全球

圖1　本屆研討會標幟

貳、汞對環境的影響

汞因其在大氣中可遠距離傳輸，且在環境中持久存在，且具生物累積性，對生態系統和人類健康都有重大負面影響，故受到全球關注。

自然環境中即有汞的排放源，如火山、土壤、海底噴口、汞豐富的地質區和森林火災，以及從淡水湖泊，河流和海洋的逸散；然而，人類活動增加了大氣中的排放，包括燃煤發電廠、金屬冶煉及垃圾焚化等各種燃燒和工業製程；另外，我們生活周遭使用的產品如鈕扣電池，日光燈管，體溫計，調溫器，開關和繼電器，氣壓計和牙齒填充物，均可能含有汞。汞在大氣中一般以氣態的元素型態存在，經由風的吹送可以進行長距離傳輸，並在大氣中停留很長一段時間，故爲全球性污染物。某些類型的細菌和真菌可將其改變成毒性最強的形式：甲基汞。甲基汞容易在魚體內累積，尤其在掠食性魚類，如鯊魚，旗魚，和某些種類的金槍魚。汞一直存在於我們生活周遭，無論是家用物品以及醫療設備都有汞的存在，然而，汞對環境影響遠超過它所提供我們的益處。

參、會議議程

會議爲期 5 天，除口頭報告外，並有海報區及廠商展覽區，相關內容十分豐富多元。

一、議程：

每日上、下午各有 7 場次口頭報告，議題包含汞排放控制技術、法規、大氣汞監測、海洋系統循環、海生動物與人體健康風險等（議程詳如表 1）。

表 1 會議議程

Room	Monday (29/07/2013)	Tuesday (30/07/2013)	Wednesday (31/07/2013)	Thursday (01/08/2013)	Friday (02/08/2013)
Pentland	Panel 1- policy/health/ monitoring P01 (Time:08:30-10:30)	Panel 2- human P02 (Time:08:30-10:30)	Panel 3-sources and industry P03 (Time:08:30-10:30)	Atmospheric mercury G06	Atmospheric mercur G08
Sidlaw	The state of mercury science in Canada and how it informs policy - the Canadian experience S16	Development of a Global Mercury Observation System S12	Analytical methodologies G01	Mercury stable isotope biogeochemistry G02	Mercury bioaccumulation and trophic transfer G20
Fintry	Mercury in marine ecosystems G23	Environmental Biogeochemistry - field approaches G14	Environmental Biogeochemistry - lab and experimental approaches G17	Environmental Biogeochemistry - lab and experimental approaches G18	Mercury regulatory issues and policy G29
Tinto	Organisms, pathways and regulations behind biological methyl-mercury production from the cell to the ecosystem S06	Fixing the world's biggest mercury problem: artesanal and small scale gold mining S20	Mercury in Polar ecosystems G27	Health effects of mercury: the child cohort studies in the Faroe Islands S23	Mercury activities in China and the lessons that can be shared S10
Moorfoot	Control technologies G09	Mercury and climate change G28	Mercury in the oil and gas processing industry S04	Defining natural and anthropogenic mercury impacts S17	Mercury chemistry interactions affecting exposure risks and health effects (eg Se, fatty acids, PCBs) G16
Kilsyth	Human exposure and risk assessment methods G25	Control technologies G10	Mercury contamination in rice agriculture: a growing global threat to human and wildlife health? S05	Contaminated sites G11	Mercury in marine mammals and human health risk S15

Room	Monday (29/07/2013)	Tuesday (30/07/2013)	Wednesday (31/07/2013)	Thursday (01/08/2013)	Friday (02/08/2013)
Plenary			“Global change and mercury cycling.” David P Krabbenhoft U.S. Geological Survey (Time:11:45 - 12:30)		
AFTERNOON					
Plenary	"The UNEP Convention - from treaty to action" Fernando Lugris, Chair INC UNEP, plus reps from free nations facing challenges Lesley Sloss, IEA Clean Coal Centre (Time:14:00 - 15:00)	“Advances in analytical technology - what is available and what is needed?” Milena Horvat, Josef Stefan Institute (Time:14:00 - 15:00)			
Pentland	Sources and emissions of mercury G04	Sources and emissions of mercury G05		Atmospheric mercury G07	
Sidlaw	UNEP Global Mercury Partnership: Efforts to Reduce Mercury Pollution from Products and Processes S24	Environmental Biogeochemistry - field approaches G15		Mercury stable isotope biogeochemistry G03	
Fintry	Mercury exposure and effects in fish and wildlife G21	Development of a Global Mercury Observation System S13		Defining natural and anthropogenic mercury impacts S18	

Room	Monday (29/07/2013)	Tuesday (30/07/2013)	Wednesday (31/07/2013)	Thursday (01/08/2013)	Friday (02/08/2013)
Tinto	Mercury in marine ecosystems G24	Human health efffects inluding ASGM exposure S21		Health effects of mercury: the Seychelles Child Development Study perspective S22	
Moorfoot	Fixing the world's biggest mercury problem: artesanal and small scale gold mining S19	Traceability of mercury measurements S08		Contaminated sites G12	
Kilsyth	Human exposure and risk assessment methods G26	Mercury exposure and effects in fish and wildlife G22		Mercury bioaccumulation and trophic transfer G19	
Ochil	Development of a Global Mercury Observation System S11	What do we know about marine methylmercury dynamics? S07		Environmental Biogeochemistry - field approaches G13	

二、廠商展示：

本次會議聚集全球頂尖汞監測設備商，包含 Tekran、Brooks Rand Instruments、PS Analytical 等，現場配置如圖 2。

其中 Tekran 於現場展示大氣汞自動連續監測設備 2537Xi，爲目前國際間唯一可進行大氣汞物種分析的自動連續監測設備，有助於解析高濃度污染成因。對於排放源的汞排放監測，美國於 2012 年 2 月通過之電力設施汞及有害空氣污染物排放標準（Mercury and Air Toxics Standards），除燃油鍋爐不論新設或既存均可用 Method 30B（半自動式之吸附管監測系統，sorbent trap）以外，

燃煤鍋爐和燃煤鍋爐和煤炭氣化複循環發電電廠（Integrated Gasification Combined Cycle）新設者只能用 cems（自動連續監測）或半自動式之吸附管監測系統（sorbent trap），既存的針對排放量小的鍋爐，可使用 Method 30B（即爲 sorbent trap）採樣 30 天。因應此規定，多家業者發展較自動連續監測費用低的半自動式之吸附管監測系統（sorbent trap），亦於現場中展示。

Exhibition Floorplan

ABLE Instruments & Controls Ltd	16
Analytik Jena UK	25
Apex Instruments	17
Arizona Instrument LLC	16
Axens	3a
BioDiversity Research Institute	35
Brooks Rand Instruments	3
Cabot Norit Activated Carbon	15
Cetac	21 & 22
Clean Air Engineering	28
Durag Group	26
econ industries GmbH	12
Environnement SA	11
Gasmet Technologies Oy	24
Intertek	3c
Jacobi Carbons	42
M&C TechGroup	33
Mercury Instruments GmbH	39
Mercury Safety Products Ltd	38
Milestone	27
Nalco Air Protection Technologies	30
National Institute for Minamata Disease	8 & 9
Nippon Instruments Corporation	6 & 7
Oak Ridge National Laboratory	10
Opsis	23
PCME	2
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Teledyne Leeman Labs	29 & 31
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圖2　展覽區配置圖

肆、研討會內容摘要

本次會議內容多元，從汞排放、大氣監測、植物分析、海洋監測至暴露評估及分析技術均有許多相關研究，而汞排放及大氣監測之相關研究較多。

一、汞排放研究

汞排放研究包含排放量推估、控制技術分析、檢測方法：

（一）汞排放量推估（此方法彙整於 UNEP, Technical Background Report for the Global Mercury Assessment, 2013，並於會場發放給與會人員）

2008 年聯合國環境總署推估 2005 年之全球汞排放量，推估主要方式係以活動強度配合檢測結果推估之排放係數，據以計算排放量，而檢測結果所表現的是控制後的排放係數，即 2008 年所推估的排放量爲控制後之排放量。後續，聯合國環境總署提供汞排放量計算工具，除過去所使用之排放係數以外，考量各國法規及產業情形不同，其排放係數亦有所差異，故增加輸出方案（output scenario）及排放入大氣之比例（分配係數，distribution factor）來進行修正，以計算排放入大氣量。

2011 年北極監測及評估小組（Arctic Monitoring and Assessment Programme, Norway）進行 2010 年全球汞排放量推估更新時，增加了蓄意使用之汞排放源，由汞消費量進行質量平衡計算全球汞排放清冊。此外，亦把過去未納入之主要排放源：小型金礦開挖（small scale gold mining, ASGM）納入排放清冊推估。爲更準確推估汞排放量，2010 年排放量推估採用質量平衡概念進行，並以未控制排放係數先進行未控制排放量推估，再依不同控制技術、不同去除效率計算控制之減量，將未控制排放量減去控制之減量，即可得控制後排放至大氣之汞排放量。

依據聯合國環境總署（UNEP）於 2008 年發布之全球大氣汞評估技術背景報告（Technical background report to the global atmospheric mercury assessment）顯示，2005 年之全球汞排放量約爲 1,480 公噸/年，主要排放源爲石化燃料燃燒（燃煤鍋爐爲主），並敘明台灣汞排放量爲 14.3 公噸/年，其中燃煤鍋爐排放量即高達 12 公噸/年；2010 年之汞排放量推估結果，台灣汞排放量爲 5.49 公噸/年，雖仍與我國推估結果有差距，但已較 2005 年版本大幅下降。聯合國環境總署 2008 年調查報告推估排放量之排放係數雖與我國（環保署）執行實際調查之數據有相當大差異，其中影響最大部份應是煤燃燒部份，由於聯合國環境總署推估過程，並未詳細蒐集各國煤源實際含量係數，致國內、外推估排放量結果有相當大差異性。

2010 年全球汞排放量推估結果顯示，人爲排放源中，以小型金礦開採之排放比例最大，其次爲煤燃燒、水泥窯及非鐵金屬冶煉。我國並無小型金礦開採，故汞排放控制可著重在煤燃燒、水泥窯等行業之管制。

（二）汞排放控制技術

本次研討會對燃煤電廠汞排放控制技術有許多研究成果，尤其以中國大陸的研究最多。目前世界各國所採用的燃煤電廠空氣污染物排放控制設備最完整者爲脫硝設施（SCR）+靜電集塵器（ESP）+排煙脫硫設備（FGD）或脫硝設施（SCR）+半乾式脫硫（SDA）+袋式集塵機（FF）。另外，中國燃煤之汞含量較我國使用之印尼煤、澳洲煤高，鍋爐出口汞濃度亦偏高，爲使煙囪排放濃度下降，空氣污染防制設備需有更高之汞去除率；由中國大陸之研究結果可看出，中國燃煤電廠汞去除效率較低（ESP：24%、ESP+WFGD：73%、ESP+CFB-FGD+FF： 66%），若僅採用靜電集塵器（ESP），去除率甚至僅有 10%以下（我國約可達 87%~88%）。

爲去除汞，中國多在燃煤進鍋爐前於其表面噴溴，以增加元素汞氧化爲 2 價汞的比例，並利於後續於排煙脫硫設備（FGD）去除，但此

方式一直有鍋爐是否會被腐蝕的疑慮，而本次會議已有研究提出有腐蝕案例，但只需於鍋爐後熱交換器前較高溫度噴入溴，即可避免腐蝕情況。美國則較常採用溴化活性碳，於防制設備後端噴入，以氧化並吸附汞，實廠測試結果顯示，去除效率均可達 90%以上。

對燃煤電廠而言，需注意之污染物除汞以外，尚有氮氧化物、粒狀物、硫氧化物，如何採取最經濟有效的控制設備，對電廠是重要課題。聯合國環境總署於 2010 年即已編撰燃煤電廠汞排放控制指南（Process Optimization Guidance for Reducing Mercury Emissions from Coal Combustion in Power Plants），提供選擇控制設備之決策方式，建議之空氣污染防制設備包含靜電集塵器（ESP）、袋式集塵器（FF）、濕式排煙脫硫設備（wet FGD）、選擇性觸媒還原設備（SCR）、乾式吸收塔（SDA）等，並提供各防制設備之相對成本，做爲選擇之參考。

（三）汞排放檢測技術

美國針對電力設施訂定汞及有害空氣污染物排放標準(Mercury and Air Toxics Standards)，除燃油鍋爐不論新設或既存均可用 Method 30B（半自動式之吸附管監測系統，sorbent trap，採樣設備如圖 3）以外，燃煤鍋爐和煤炭氣化複循環發電電廠（Integrated Gasification Combined Cycle）新設者只能用自動連續監測（cems）或半自動式之吸附管監測系統（sorbent trap）。

汞的排放包含粒狀汞、元素汞及二價汞，其污染物之排放及測定過程較爲複雜，與其他空氣污染物自動連續監測系統（cems）相比，汞的自動連續監測系統之設置及維護費用較高，近年已有越來越多商業化的半自動式之吸附管監測系統（sorbent trap），該設備可裝置在煙囪長期採樣，污染源只需定期更換吸附管，將換下的吸附管送至實驗室分析，即可得該排放源長時間之平均排放濃度值，但無法了解其間濃度變化情

形以及是否有瞬時高値之情形。至於汞之自動連續監測設備（cems）亦已商業化多年，優點爲可獲得排放源即時排放濃度，了解排放量變化情形，惟該設備之費用較半自動式之吸附管監測系統（sorbent trap）高。

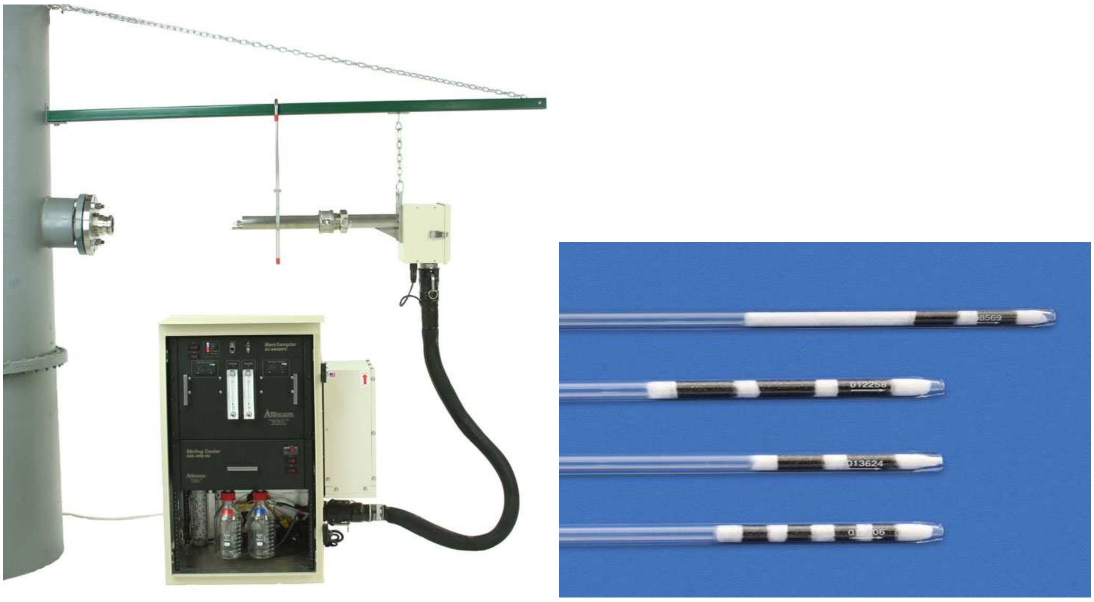

圖3　半自動式之吸附管監測系統（sorbent trap）採樣設備圖

二、大氣汞監測

依據聯合國環境總署於 2013 年發布之全球大氣汞評估技術背景報告顯示，由於汞有全球傳輸特性，故世界各國多有進行大氣汞的監測，監測結果彙整如下：

（一）歐洲

近 20 年來，在愛爾蘭的戈爾韋大氣測站（Mace Head, Galway, Ireland，可視爲未受當地排放源污染的背景測站）執行大氣汞監測，結果顯示，大氣總汞濃度呈現下降趨勢。由 Mann-Kendall test 和 Sen’s slope 預測，1996 年大氣總汞背景濃度之基線值爲 1.82 ng/m^3，下降至 2011 年之 1.40 ng/m^3。統計變化趨勢爲-0.027 ± 0.01 ng/m^3/y，亦即每年降低 1.4 – 1.8%，或 16 年來降低 26%。

2009 至 2011 年在德國背景測站 Waldhof 監測元素汞（GEM）、氧

化汞（GOM）和粒狀物結合汞（TPM、PBM$_{2.5}$），由監測結果可看出，日平均值最小、最大值分別爲 1.1 ng/m^3 和 3.1 ng/m^3。3 年濃度之中位數爲 1.63 ng/m^3，與北半球背景濃度 1.7 ng/m^3 相近。元素汞、粒狀物結合汞（粒徑小於 2.5 μm）之年平均值的變化情形不顯著，但氧化汞似乎有上昇趨勢，惟只有 3 年資料，後續仍需持續監測方有統計意義。

粒狀物結合汞（粒徑小於 2.5 μm）在冬季的濃度變化大於夏季，可能原因爲冬季使用暖氣設備，而此濃度值與 PM$_{2.5}$ 有相同月變化趨勢。氧化汞的日變化比其他汞物種明顯，中午較高，可能原因爲光化作用造成汞氧化。

（二）北美洲

加拿大及美國均有國家汞監測網，在一般情況下，加拿大大氣汞濃度約爲 1-2 ng/m^3，以晚冬較高，夏季較低，而白天的最高濃度通常發生在靠近正午時，最低濃度則多發生在日出前。美國全球大氣汞監測網之監測結果顯示，元素汞年平均值爲 1.2 到 2.1 ng/m^3，最高濃度發生在市區和郊區，且在這些測站，氧化汞（GOM）和粒狀物結合汞（粒徑小於 2.5 μm）的濃度年平均值變化較大。然各測站的物種變化濃度並無一致趨勢，主要原因是汞物種濃度受排放源，大氣傳輸，化學循環和沉積過程等影響，前述因子在各測站各有不同。

（三）亞洲

中國大陸學者進行許多地區之監測，最受矚目者爲貴陽地區，該地區之地質特殊，大氣中總汞濃度達 8.4±4.87 ng/m^3，遠高於其他地區之監測結果。其他城市如上海，其濃度約爲 2.7±1.7ng/m^3，可能與該地區近海，可能有交換海上較乾淨之空氣，而使得汞濃度下降。南韓之監測結果顯示，過去 10 年來大氣汞濃有明顯下降趨勢；首爾監測結果與中國大陸沿海城市如上海及寧波相近；亞洲偏遠地區大氣汞監測濃度約爲

1.7-4.6 ng/m^3，高於北半球背景值（1.5-1.7 ng/m^3）；黃海接壤中國大陸東部和朝鮮半島，這是東亞地區重要的汞源之一，在此區域監測結果顯示，大多數高汞濃度事件發生在靠近東中國大陸的測站，推論含汞氣團從大陸流出。

（四）由於汞有全球傳輸特性，全球應致力於一同維護環境降低汞危害，聯合國環境總署歸納出未來大氣汞監測及研究之方向如下：

1. 爲使研究結果發揮最大效用，全球監測結果應相互交流並於必要時進行監測計畫之協調。此外，遠距離傳輸對排放源和受體解析有影響，應進一步進行對流層汞含量研究，以了解對流層中汞垂直分布情形，減少預測之不確定性。
2. 汞與大氣中氧化劑的氧化還原反應機制尚需要進一步調查，雖然目前還沒有共識，但目前了解溴爲重要物質，需進一步了解其在氧化還原反應中的重要性。
3. 汞化合物中，對人體有危害者爲甲基汞，大氣中汞沈降後如何甲基化並進入生物體內透過食物鏈進入人體，爲重要領域，需進一步調查。
4. 汞化合物在海洋、空氣、土壤和植被的轉換情形尚不完全清楚，應進行相關研究以了解機制。

伍、心得與建議

一、 由於汞爲全球性議題，世界各國均投入許多研究、監測與管制，本署近年來亦持續執行國內排放源檢測與環境監測之工作，對國內排放量及環境現況已有相當掌握，國內汞排放量變化不大，平均約 1.36 公噸/年。然聯合國環境總署推估我國之汞排放量極高，以及部分國內學者於局部區域監測到汞濃度高值即發表於國際期刊，易使國際間對我國實際情況

產生誤解，建議未來可考量適時將成熟之成果發表於國際期刊，以釐清國際及外界之誤解。

二、依本署推估之排放資料庫結果顯示，我國汞排放量較大行業爲電力業，爲加強管制空氣中汞之排放量，我國102年1月21日預告之電力設施空氣污染物排放標準草案已參考國際管制經驗及國內排放現況，增訂燃煤電廠汞排放標準，其中既存污染源標準訂爲5μg/Nm^3，新污染源標準訂爲2μg/Nm^3；另參考美國針對電力設施訂定汞排放檢測規範，電力設施之汞排放檢測，已有規範應裝設自動連續監測（cems）或半自動式之吸附管監測系統（sorbent trap），建議未來電力業排放標準草案發布施行後，可於了解我國電廠實際排放濃度、連續監測技術、設置成本等資訊後，評估訂定電力業汞連續監測規範之可行性，以落實排放標準之管制。

附錄

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AMAP

Technical Background Report for the Global Mercury Assessment

2013

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Produced by
Arctic Monitoring and Assessment Programme
AMAP Secretariat
Gaustadalléen 21
N-0349 Oslo
Norway
Tel. +47 22 95 83 40
Fax +47 22 60 44 27
amap@amap.no

and

United Nations Environment Programme (UNEP)
Division of Technology, Industry and Economics (DTIE)
Chemicals Branch
International Environment House
11-13, Chemin des Anémones
CH-1219 Châtelaine (Geneva)
Switzerland
Tel: +41 (0) 22 917 81 85
Fax: +41 (0) 22 797 34 60
Email : metals.chemicals@unep.org
http://unep.org/hazardoussubstances/

The report can be found on the AMAP website *www.amap.no* and UNEP Chemicals Branch's website: *http://www.unep.org/hazardoussubstances/Mercury/Informationmaterials/ReportsandPublications/tabid/3593/Default.aspx*

AMAP/UNEP promote environmentally sound practices globally and in their own activities. This publication is printed on paper from environmentally-managed forests, using vegetable-based inks and other eco-friendly practices. Our distribution policy aims to reduce AMAP/UNEP's carbon footprint.

Scientific, technical and linguistical editing
Carolyn Symon (carolyn.symon@btinternet.com)

Lay-out and technical production
Burnthebook Design, Derby DE24 8HR, United Kingdom (burnthebook.co.uk)

Printing
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Contents

Preface

This report details the technical background to the *Global Mercury Assessment 2013 – Sources, Emissions, Releases and Environmental Transport* (summary for policy-makers) that has been developed in response to Decision 25/5 III, paragraph 36 of the Governing Council of the United Nations Environment Programme (UNEP), that: "Request the Executive Director, in consultation with Governments, to update the 2008 report entitled "*Global Atmospheric Mercury Assessment: Sources, Emissions and Transport*" for consideration by the Governing Council / Global Ministerial Environment Forum at its twenty-seventh session."

This technical background report has been developed in collaboration with the Arctic Monitoring and Assessment Programme (AMAP). As such, this report also constitutes a contribution to the work of AMAP and the Arctic Council.

Chapter 2 of this report (*Global Emissions of Mercury to the Atmosphere*) was developed by a joint UNEP/AMAP Expert Group, building on the competence established during the AMAP/UNEP collaboration that resulted in the 2008 *Technical Background Report to the Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* report (UNEP, 2008). In producing this part of the report, considerable efforts were made to engage a wide participation of national experts from regions around the globe. Thanks to funding provided by Canada, Denmark, Japan, Sweden, Norway, the Nordic Council of Ministers, and the EU, experts from Argentina, Australia, Brazil, China, India, Japan, Mexico, Republic of Korea, South Africa and the USA actively participated in the work to develop Chapter 2 of this report. Expertise and information made available through the UNEP Partnership area on Mercury Control from Coal Combustion Information was used, as were data acquired during the preparation of the UNEP Paragraph 29 study (*Study on Mercury Sources and Emissions, and Analysis of Cost and Effectiveness of Control Measures*, UNEP 2010a). The sections concerning artisanal and small-scale gold mining were developed through cooperation with experts from the UNEP Partnership on Reducing Mercury in Artisanal and Small-scale Gold Mining and from the Artisanal Gold Council (AGC).

Chapter 3 of this report (Atmospheric Pathways, Transport and Fate) was prepared by experts from the UNEP Mercury Air Transport and Fate Research Partnership Area.

Chapter 4 of this report (Global Releases of Mercury to Aquatic Environments) was prepared by a UNEP/AMAP expert group under the leadership of experts from the Institute Jožef Stefan (Slovenia) and utilised material prepared for UNEP by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP).

Chapter 5 of this report (Aquatic Pathways, Transport and Fate) was prepared by a UNEP/AMAP expert group under the leadership of experts from the Geological Survey of Canada and the University of Connecticut and contributions from Institute Jožef Stefan (Slovenia). The input of John Munthe to this work is also greatly appreciated.

1. Introduction

Authors: Simon Wilson, John Munthe, Peter Outridge, Robert Mason

Contributor: Elsie Sunderland

1.1 Background and mandate

In 2009, UNEP's Governing Council (GC) requested that "UNEP in consultation with Governments, update the 2008 report entitled *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* for consideration by the Governing Council/Global Ministerial Environment Forum at its twenty-seventh session in 2013". (Decision 25/5 III, paragraph 36).

Building on the 2008 report, the new report entitled *Global Mercury Assessment 2013 - Sources, Emissions, Releases and Environmental Transport* should provide updated:

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

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

The main focus of the updated report is on mercury (Hg) emissions to the air and pathways and fate of atmospheric Hg. However, in response to questions raised by several governments in the Intergovernmental Negotiating Committee (INC) developing a global instrument on Hg to include releases to water, the content of the updated report has been expanded to include information on Hg releases to water and pathways and fate in aquatic environments.

This report (*Technical Background Report for the Global Mercury Assessment 2013*) provides the detailed technical background for the information and findings that are presented in the *Global Mercury Assessment 2013 - Sources, Emissions, Releases and Environmental Transport* summary report. It consists of five parts:

Chapter 1 – Introduction

Chapter 2 – Global Emissions of Mercury to the Atmosphere

Chapter 3 – Atmospheric Pathways, Transport and Fate

Chapter 4 – Global Releases of Mercury to Aquatic Environments

Chapter 5 – Aquatic Pathways, Transport and Fate

As described above, this report deals with Hg releases to the atmosphere and water, and the pathways and fate of Hg after it has entered the atmosphere and aquatic environments. Figure 1.1 illustrates these components, showing which parts of the global Hg cycle are considered in the various chapters of this report – Figure 1.1 can therefore can be viewed as a 'road map' for the report. Figure 1.2, using the same basic diagram shows, in quantitative terms, the main features of the global Hg cycle, including numerical estimates for the Hg 'storage' and flux components that are described in more detail in the following chapters.

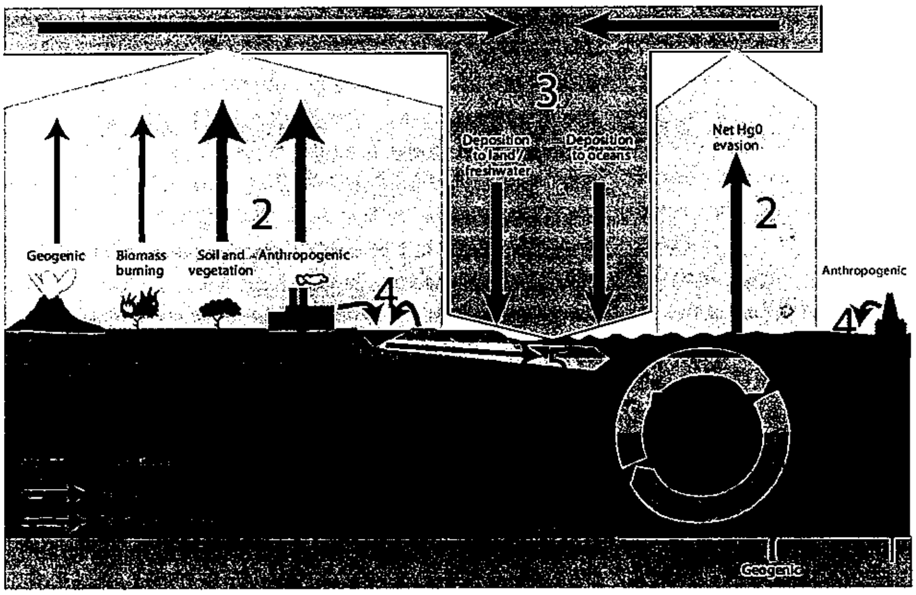

Figure 1.1. Components of the global mercury cycle as addressed in this report. Numbers refer to the chapters of this report.

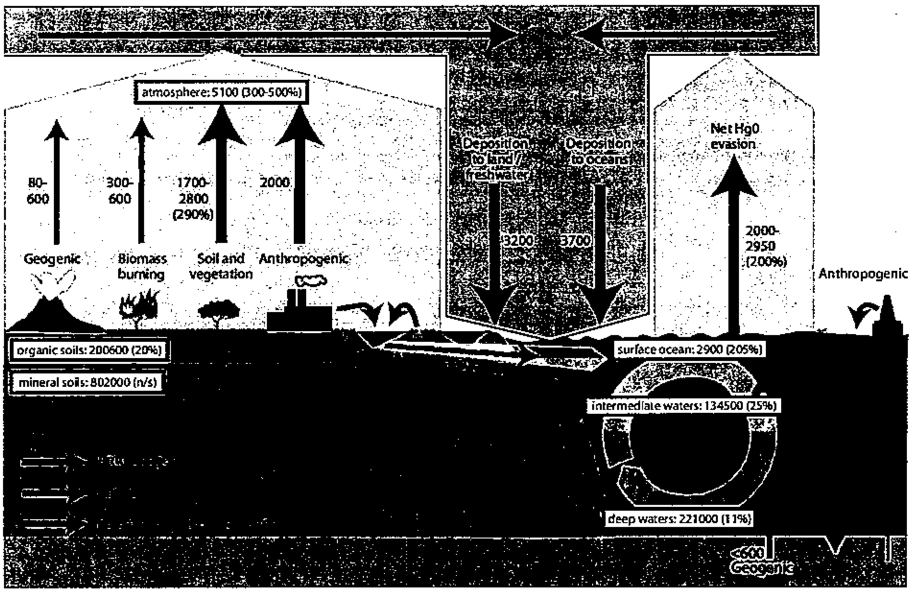

Figure 1.2. The global mercury budget. Source: adapted from Mason et al. (2012). Total inventories (numbers in white boxes) are in tonnes, and fluxes in tonnes per year. The percentage values in brackets are the estimated increases in inventories in the past 100 years due to anthropogenic activities.

1.2 Global mercury budgets

Mercury is released to the environment from natural sources and processes and as a result of human activities. Once it has entered the environment, Hg cycles between major environmental compartments – air, soils and waters – until it is eventually removed from the system through burial in deep ocean sediments and mineral soils. Methylmercury, the most toxic and bioaccumulative form of Hg which presents most health risk to humans and wildlife, is mainly produced in aquatic ecosystems through natural bacterial processes.

In order to provide a general framework for the discussions in Chapters 2 to 5 of this report, the following section presents a global Hg budget based on recent modelling work.

Owing to its scale and chemical complexity, and the lack of detailed information for many parts of the ecosystem, global-scale models provide the most practical means of describing the global Hg cycle in a quantitative manner. A number of global atmospheric Hg models exist. But until recently, only one combined atmospheric-terrestrial-oceanic model has been available, the GEOS-Chem Mercury model (Strode et al., 2007; Smith-Downey et al., 2010; Mason et al., 2012). Recent GEOS-Chem model results, as described by Mason et al. (2012), represent the current 'best estimate' of the global Hg budget. The model is constrained and generally supported by empirical data on Hg concentrations and fluxes in various environmental media, and represents a consensus which has not been challenged within the Hg scientific community.

As with all such modelled budgets, large uncertainties exist regarding both the amounts of Hg 'stored' in the different environmental compartments and the fluxes of Hg between these compartments (see Table 1.1). Most of these uncertainties are due to unknown or poorly known input parameters and process rates, as discussed in more detail in Chapter 3. Despite this fact, most global Hg models do not present uncertainty estimates on their mass balances and fluxes. Sunderland and Mason (2007) reported that 90% confidence intervals for GEOS-Chem estimates of most fluxes (i.e., for rivers, atmospheric deposition, particle settling, lateral and vertical flows) were only 2- to 4-times as large as the median or best estimate values. However, the estimates of evasion were less certain, with 90% intervals of 5–10 times the best estimate for different ocean basins. Uncertainty analysis conducted as part of new global Hg modelling work by Qureshi et al. (2011; the World Multimedia Mercury Model, WorM3) suggested that 95% estimate dispersion ranges were over an order of magnitude for most global Hg inventories and fluxes. However, the best estimates from Qureshi et al. (2011) compared well with other models. For example, Qureshi et al. (2011) estimated a net conversion of Hg0 (elemental mercury) to HgII (inorganic divalent mercury) in the atmosphere of 3000 t/y, with a 95% range of 400 to 12400 t/y. This average compares favourably with the 6000 t/y estimate using GEOS-Chem (Selin et al., 2007). The calculated atmospheric residence time of Hg0 in WorM3 was 8.2 months with a 95% dispersion of 2.4 to 24 months, which also agrees well with other estimates of 8.4 to 20.4 months (Holmes et al., 2006; Selin et al., 2007). In general, good agreement (within a factor of three) was observed for the best estimates of most global Hg compartment inventories, chemical reaction rates and fluxes, between WorM3 (Qureshi et al., 2011) and other spatially resolved global models including GEOS-Chem (Lamborg et al., 2002; Selin et al., 2008; Sunderland and Mason, 2007; Soerensen et al., 2010; Smith-Downey et al., 2010). The largest potential errors in the GEOS-Chem model, in the context of the aquatic Hg cycle, may concern air-water gas exchange, specifically: (i) the mechanisms of the redox reactions in surface oceans, as defined by the amount of reducible Hg present in surface oceans, and rate constants for reduction and oxidation of Hg species by various pathways; (ii) atmosphere-water Hg mass transfer processes as defined by wind velocity; and (iii) Hg species inter-conversion reactions in the atmosphere (Qureshi et al., 2011). It was estimated that these uncertainties may contribute more than errors in anthropogenic emission estimates to the total uncertainty in modelled atmospheric concentrations and deposition fluxes.

Table 1.1. Estimates of environmental mercury fluxes. Source: updated from AMAP/UNEP (2008).

Hg fluxes, t/y	Selin et al., 2007	Soerensen et al., 2010	Holmes et al., 2010b	Mason et al., 2012
Natural emissions from land to atmosphere	900		500	80–600
Natural emissions to oceans				< 600
Anthropogenic emissions	2200		2100	2000
Re-emissions from land	1500		1700	1700–2800
Emissions from biomass burning			300	300–600
Re-emissions from ocean	2400	2900	3700	2000–2900
Total sources	**7000**		**7800**	**6100–8900**
Deposition to land			3000	3200
Deposition to ocean		3700	5300	3700
Total deposition	**7000**		**8300**	**6900**

Notwithstanding these uncertainties, such budgets provide a useful framework for describing the structure of the material in this report and also for explaining the way that anthropogenic releases impact on the Hg cycle.

Total annual Hg emissions to the atmosphere have been estimated at up to 8900 t/y (see Table 1.1). The budget of Mason et al. (2012) estimates current Hg emissions to the atmosphere from natural and anthropogenic sources at about 80–600 t/y and about 2000 t/y, respectively, with re-emissions making up the remainder. The indicated anthropogenic flux value of 2000 t/y is an approximate estimate; a detailed quantification of current (2010) Hg emissions to air from anthropogenic sources is the subject of Chapter 2 of this report.

Comparing pre-industrial and post-industrial emissions from all sources, Sunderland and Mason (2007) concluded that human effects on the Hg cycle have resulted in about three-times as much Hg being emitted to the atmosphere now than in the pre-industrial period. Anthropogenic emissions increased significantly following the (European) industrial revolution around 200 years ago, and are likely to have peaked sometime in the late 20th century. As more countries experience industrial development, resource exploitation continues. However reductions in atmospheric Hg emissions have also occurred due to changes in fuel use and co-benefits from improved emission control technologies for major air pollutants (particles, sulphur oxides and nitrogen oxides) at major emission sources such as power stations and industrial plants, as well as the introduction of Hg-specific controls at some facilities and reduced use of Hg in products and some industrial processes.

Estimates of current annual emissions associated with some re-emission components have been quantified on the basis of studies involving measurements as well as models. For example, emissions from biomass burning, which includes both natural wildfires and anthropogenic (agricultural and other) biomass burning were estimated at ~ 675 ± 240 t/y (Friedli et al., 2009). In the case of biomass burning, much of the Hg emitted to the atmosphere is likely to be associated with re-emission of Hg previously deposited onto vegetation surfaces, with a small fraction from Hg uptake from soils by root systems. Similarly, fast re-emission of Hg from ice and snow following atmospheric mercury depletion events (AMDEs) has been estimated to re-emit up to 80% of the atmospheric deposition in the Arctic associated with AMDEs (AMAP, 2011). However, estimates for the most significant re-emission components – re-emissions from soils/vegetation and evasion from ocean surface waters – are derived mainly from models. Through their parameterisation of geochemical processes, these models attempt to balance budgets and residence times of Hg in various components of the geosphere, in a manner that is consistent with observed levels of Hg in different media. Oceanic re-emissions have been measured during cruises in most of the world's major oceans but these results only cover limited geographical and temporal scales and thus need to be scaled up to derive global estimates. Recent publications that present global Hg budgets based on the GEOS-Chem budget model imply annual re-emissions to air from soils and oceans of 1700–2800 and 2000–2950 t/y, respectively (Mason et al., 2012, Figure 1.2). The budget presented by Holmes et al. (2010b) has corresponding re-emission estimates of 1700 and 3700 t/y, respectively. The natural (geogenic) emissions from land (mainly volcanic emissions) are estimated to be 80–600 t/y. Natural sources also release Hg to the ocean through sub-surface vents, however this contribution (estimated at <600 t/y) is believed to be largely retained around the location of the vents and therefore only a small part of this release enters the water column.

Other types of model employed to simulate Hg atmospheric transport include somewhat lower estimates of Hg emissions to the atmosphere from natural and re-emission sources of 3500 t/y (GRAHM model, AMAP, 2011) and 4230 t/y (GLEMOS model, AMAP, 2011). Estimates of natural emissions and re-emission of Hg to the atmosphere thus are subject to considerable uncertainty. This report uses the budget numbers of Mason et al. (2012) as a basis for discussions because they are the most recent, building on previous budgets by Soerensen et al. (2010) and Holmes et al. (2010b). They are also the most comprehensive yet published in terms of coverage of Hg fluxes and inventories in different environmental compartments.

2. Global Emissions of Mercury to the Atmosphere

Authors: Simon Wilson, Karin Kindbom, Katarina Yaramenka, Frits Steenhuisen, Kevin Telmer, John Munthe

Contributing authors: Leila Devia, Tomas Gustafsson, Wojciech Jozewicz, Ragini Kumari, Joy Leaner, Jacob Maag, Otávio Luiz Gusso Maioli, Peter Maxson, Peter Nelson, Jozef Pacyna, Deepak Pudasainee, Yong Chil Seo, Lesley Sloss, Gustavo Solorzano, Madeleine Strum, Kyrre Sundseth, Noriyuki Suzuki

Contributors: Lars Petter Bingh, Paul Bunyana, Sergio Cinnirella, Petra Hagström, Yoshihiro Inoue, Allan Kolker, Artemis Kostareli, Vagner Maringolo, Nicloa Pirrone, Gregory Scott, Shuxiao Wang

2.1 Sources of mercury emissions to the atmosphere

2.1.1 Natural, anthropogenic and re-emission source categories

As discussed in the 2008 *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* report (UNEP Chemicals Branch, 2008), current Hg emissions to the global atmosphere come from three types of source: new emissions from **natural** (i.e., geogenic) sources, new emissions from **anthropogenic** sources, and **re-emission** of historically-deposited Hg which originally came from both anthropogenic and natural sources.

Natural sources – mercury released from the Earth's crust by the continuous and ubiquitous natural weathering of Hg-containing rocks or by geothermal activity, or Hg emitted during episodic events such as volcanic eruptions. Over the past hundreds to thousands of years, Hg emissions from natural weathering globally can be assumed to have been fairly constant, with variations largely associated with changes in volcanic and geothermal activity (see Figure 2.16 later in this chapter). Current annual (geogenic) releases to air from natural sources are estimated at around 80–600 t/y (Mason et al., 2012, see Figure 1.2) and 300 t/y (Corbitt et al., 2011).

Anthropogenic sources – mercury released as a result of current[1] human activities. Anthropogenic sources result in Hg emissions to the atmosphere (discussed in this chapter) and Hg releases to aquatic systems (considered in Chapter 4). Estimates of current anthropogenic emissions to the atmosphere are around 2000[2] t/y. Section 2.2 presents a detailed inventory of current anthropogenic emissions to air totalling 1960 (1010–4070) t/y in 2010.

Some anthropogenic sources release Hg as a result of man's use of mineral resources as fuels and as raw materials in industrial processes, including metal production, in particular processes that involve heating materials to high temperatures. These sources involve human activities that (intentionally or unintentionally) release Hg from crustal rocks and/or expose rocks and ore bodies that would otherwise remain buried to surface weathering processes. Mercury is present as an impurity in fossil fuels (coal in particular), ores mined for ferrous and non-ferrous metal production and other minerals used in the production of materials such as cement. Although the Hg is generally present in low concentrations, the considerable volumes of these materials that are extracted and used and the high temperature processes involved can result in substantial Hg releases to the atmosphere. Mercury is itself produced commercially by mining and extraction of Hg ore (cinnabar), however, compared with other primary anthropogenic sources, Hg production is a minor component. Because the environmental releases of Hg associated with these activities are an artefact of the processes involved, the associated emissions are sometimes termed 'by-product' or 'unintentional' emissions. Many industrial sites such as old mines and decommissioned chlor-alkali plants exhibit high levels of local Hg contamination, and Hg emissions from these contaminated sites can continue for long periods after operations have ceased.

A second category of anthropogenic sources are those that release Hg to the atmosphere following its intentional use. These intentional uses include Hg use in artisanal and small-scale gold mining (ASGM) and certain industrial and chemical processes, and in man-made products that contain Hg. These products include certain types of energy saving and fluorescent lamps, batteries, electrical devices and instruments (including Hg thermometers), paints, cosmetics, and some pesticides and fungicides. Releases occur during manufacturing, and following breakage and/or disposal of Hg-containing products. Associated anthropogenic sources include releases from (controlled and uncontrolled) incineration of waste, and from wastes in (contained) landfills or (uncontained) dumps, or contaminated sites. Recycling of materials, including secondary ferrous metal production, results in some Hg emission, as does Hg use in dental amalgams where cremation of human bodies results in release of Hg from dental fillings to the atmosphere. One of the human uses of Hg with the highest associated Hg emissions is its use for extracting gold in ASGM. Mercury emissions to the atmosphere also occur from its use in the chlor-alkali industry in Hg-cell caustic soda production. Use of Hg in the production

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[1] Current in this discussion refers to the current year; current emissions are therefore those that take place within the current annual period, as opposed to historical or past emissions that took place at some point in time before the current annual period.

[2] Global inventories, in particular past global inventories of anthropogenic emissions to air do not necessarily include all relevant sectors and activities. There will therefore be additional anthropogenic emissions from sectors not quantified. The most recent inventories, including that presented in this report are assumed to cover the most important anthropogenic emission sectors/activities; sectors that are not addressed include those identified in Section 2.2.4.2.

of vinyl chloride monomer (VCM) is a potentially significant source for which emissions are still not quantified.

Re-emissions – these comprise Hg releases to the atmosphere that are derived from past natural and anthropogenic releases. Under the right conditions, Hg can be (re-)emitted to the atmosphere from the Earth's surfaces (soil, rocks, snow and ice, surface waters – including ocean surface water, and vegetation) that have previously received Hg either from atmospheric deposition or through another transport pathway. Re-emission sources tend to be diffuse and are associated with 'environmental reservoirs' of Hg that have accumulated over time, particularly in organic surface soils and surface ocean waters.

Estimates of current annual re-emissions to the atmosphere that are a legacy of historical Hg releases from both anthropogenic and natural sources are in the range 4000–6300 t/y (Mason et al., 2012; see Section 1.2).

An important fact to remember concerning re-emission sources is that the origin of the re-emitted Hg is both natural and anthropogenic. Re-emitted Hg has been deposited at some point in the past and the original release sources can no longer be distinguished. Releases of Hg associated with anthropogenic activities have increased dramatically since humans started to use Hg over 1000 years ago, but especially with the onset of significant burning of fossil fuels that started with the (European) industrial-revolution in the 19th century, and the widespread use of Hg in gold and silver mining in other regions. This has loaded the environmental reservoirs – thus enhancing re-emission sources. A major reason, therefore, for controlling current anthropogenic Hg emissions is to reduce this 'input' so that environmental reservoirs of Hg can be gradually depleted by natural processes that 'permanently' remove Hg from the system (such as burial in deep sea sediments). Controlling anthropogenic Hg emissions therefore reduces present-day emissions and also acts to reduce (future) re-emission from environmental reservoirs of Hg. Controlling current anthropogenic emissions is thus the only option for limiting the amount of 'new' Hg entering the global biogeochemical cycle.

For the reasons discussed above, it is important that re-emission sources, despite the fact that they are associated with natural Hg environmental cycling processes, are not considered to be a component of 'natural' emissions, which is how they have been treated in some studies. Although the (original) sources of the Hg that enters the air through re-emissions cannot be identified as natural or anthropogenic, it is also important to recognise that human activities can enhance re-emissions. Examples of ways human activities can enhance re-emissions include: intentional biomass burning (as opposed to natural wildfires); coal bed fires started accidentally during human activities (as opposed to natural fires); and potentially as a result of (human induced) climate change (e.g., increased wildfires, thawing of permafrost and increased microbial activity that impacts Hg cycling).

It is not yet clear how climate change will affect the balance between Hg atmospheric deposition and re-emissions. This may vary regionally as, for example, sea-ice cover decreases in some areas and precipitation increases or decreases in others; however, independent of other factors, it is expected that rising temperatures would be likely to increase the re-emission of (semi-)volatile substances such as Hg from the Earth's surfaces to the atmosphere. On this basis, it also follows therefore that decision-makers can instigate actions that can decrease re-emissions – by reducing the anthropogenic sources that add Hg to environmental reservoirs but also through other actions that may mitigate conditions that promote re-emissions.

One consequence of the large reservoirs of Hg already in the environment is that there is likely to be a time-lag of at least decades, depending on the reservoir, before emissions reductions have a demonstrable effect on Hg levels in human food-chains (other than in situations involving high local contamination). This is particularly so for Hg levels in marine food chains. It is imperative, therefore, that international efforts to reduce current emissions begin as soon as possible, because delays in action now will inevitably lead to future delays in noticeable reductions of Hg in the world's ecosystems.

2.1.2 Global mercury budgets and estimates of emission from natural and re-emission sources

As described in Section 1.2, total annual Hg emissions to the atmosphere have been variously estimated at between 5500 and 8900 t/y. Current Hg emissions to the atmosphere from natural sources are estimated at ca. 80–600 t/y (Mason et al., 2012). Mercury is emitted from volcanoes primarily as gaseous elemental mercury (GEM). Estimates of Hg emissions from volcanoes are generally based on the Hg/SO_2 (mercury / sulphur dioxide) ratio, with ratios of 1.18×10^{-5}, 1.16×10^{-5} and 5.88×10^{-6} suggested for erupting volcanoes, continuously degassing volcanoes and ash rich plumes, respectively (Ferrara et al., 2000a; Nriagu and Becker, 2003; Mather and Pyle, 2004). Mercury emissions from calderas may also represent an important natural source of Hg (Ferrara et al., 1998). Lack of relevant data and order of magnitude variation in some of the factors involved mean that these estimates are highly uncertain (Pyle and Mather, 2003; Mather and Pyle, 2004).

Re-emissions from soils and vegetation and from oceans are estimated at ca. 1700–2800 t/y and 2000–2950 t/y respectively (Mason et al., 2012), corresponding to about 60% of total annual emissions to the atmosphere. Re-emissions from land and vegetation are about twice those from oceans on a unit area basis. Due to its volatility, GEM is an important component in the cycling of Hg between soil and air and several studies have shown that Hg volatilisation increases with increasing soil moisture content (Schlüter, 1993; Steinnes, 1997; Kabata-Pendias and Mukherjee, 2007). Mercury in soils can be converted to methylated forms and transported to aquatic ecosystems, contributing to total methylmercury loading and bioaccumulation.

Mercury accumulates in vegetation mainly through uptake from the atmosphere and atmospheric deposition to foliage (Rea et al., 2002). The atmospheric contribution to the total Hg content of the leafy parts of plants is of the order of 90–95% and 30–60% for roots (Mosbaek et al., 1988; Eriksen et al., 2003; Eriksen and Gustin, 2004). Mercury uptake from soils appears to be insignificant (Lindqvist et al., 1991; Schuster, 1991; Grigal, 2003; Karpinska, 2005). Biomass burning (from wildfires and agricultural burning) has been estimated to contribute 675 ± 240 t/y of Hg to the atmosphere (Friedli et al., 2009), with a strong seasonality depending on the emission region concerned. This value is close to the estimate used in global budget models. Much of this therefore constitutes a re-emission of previously deposited atmospheric Hg.

Re-emissions from oceans constitute more than 96% of re-emissions from the Earth's surface waters (Mason et al., 2012); the remainder is from lakes and other surface waters. There is a significant latitudinal gradient of GEM evasion from tropical to polar oceans, with annual means ranging from ~33 ng/m^2/d near the equator to ~3 ng/m^2/d at 60° N (Strode et al., 2007). This pattern is believed to reflect regional changes in average biological productivity and sunlight irradiance. Mid-latitude evasion displays a large seasonal cycle induced by biological productivity. Ocean evasion rates are also elevated downwind of industrial regions (e.g., Pirrone et al., 2003). Rates of evasion can be very high in shallow waters such as the Mediterranean Sea, where rates vary from about 60–190 ng/m^2/d in different sectors from open waters to coastal polluted sites (Gårdfeldt et al., 2003; Andersson et al., 2007). In lakes with high dissolved organic carbon and Hg content, evasion rates can reach up to 130 ng/m^2/d (Boudala et al., 2000).

Figure 2.1 illustrates the major components of the global Hg budget that introduce and remove Hg from the atmosphere (see also Figure 1.2). An important consideration to note is that reduction in the current anthropogenic Hg flux to the atmosphere (2) will ultimately reduce the related fluxes (3–5) that determine environmental Hg levels at the Earth's surface.

The United Nations Environment Programme (UNEP) has requested that this report be developed as a contribution to international efforts to reduce anthropogenic Hg emissions. Within this context, therefore, the remainder of this report focuses on (quantification of) anthropogenic Hg emissions to air rather than natural emissions. The essential points from the above discussion are that approximately 30% of current annual Hg emissions to air are due to anthropogenic sources. But as well as this, current anthropogenic emissions are continuing to load up the environmental pools of Hg that give rise to the re-emissions that account for a further 55–60% of current annual emissions to air.

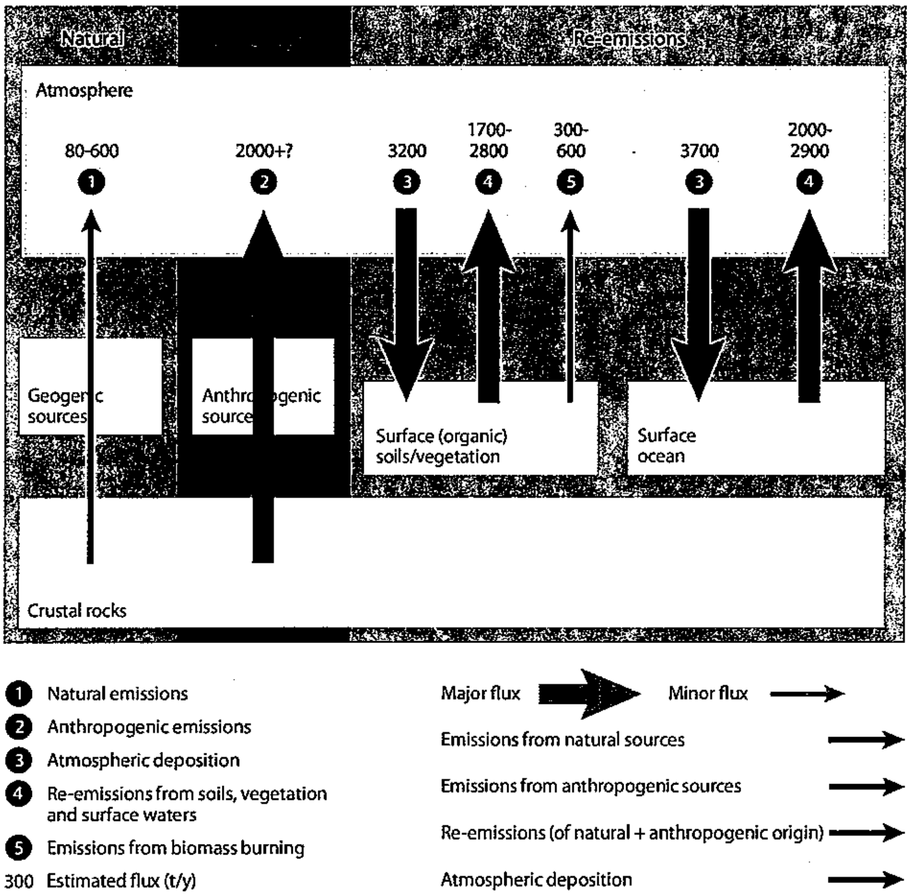

Figure 2.1. Schematic illustration of the main sources of mercury to the atmosphere showing natural, anthropogenic and re-emission components, and fluxes between the atmosphere and various surface environmental compartments. Flux estimates are in t/y as derived from Mason et al. (2012) (see also Figure 1.2).

2.2 Estimating global anthropogenic mercury emissions to air for 2008–2010: Methodology

A key component of this work to update the 2008 *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* report (UNEP Chemicals Branch, 2008; AMAP/UNEP, 2008) is the production of a new global inventory[3] of anthropogenic Hg emissions to the atmosphere. This new inventory has the target year of 2010 – however recognising that information required to produce such inventories may not yet be available for all countries, the basis for most of this new inventory is latest available data from the period 2008–2010.

2.2.1 Methods for estimating emissions

Various methods are employed to estimate emissions of Hg at the plant/facility, national, regional and global level. In general, they fall under one of two main categories:

- *Mass-balance/substance-flow based estimates*: These work on the principle of what goes in must come out. Amounts of Hg in fuels and raw materials constitute the inputs; and the outputs are the amounts of Hg emitted to air, discharged to water/land, retained in products or in wastes, or otherwise recovered and stored or disposed of. Inputs and outputs are assumed to balance and the calculation methods employed are relatively straight forward. Accuracy and precision of the estimates typically depend on the availability of the information that defines the inputs and the validity of assumptions regarding the pathways involved (i.e., whether releases are to air, water, waste-streams, etc.). Estimates made using mass-balance approaches have been characterised as low accuracy for low-level emissions, but moderate accuracy for long-term averages, moderate precision, and low-cost (Mazzi et al., 2006). Costs are higher when these include costs of analysis of fuels, raw-materials and wastes, etc.
- *Measurement-based estimates*: These rely on measurements made at appropriate points in the industrial process or in the product/waste output streams to define the emissions to air or releases to water, land, waste products, etc. The high costs associated with some monitoring/analysis systems mean that they are only deployed for continuous monitoring at some facilities. Many measurements-based emissions estimates therefore rely on a relatively few measurements. Accuracy and precision of the resulting estimates therefore often depends on the validity of extrapolating 'snap-shot' measurements made at infrequent intervals to longer periods, or measurements made at 'representative' plants to other facilities with similar operations. Emission estimates that apply to an entire year (or even shorter periods) will depend on how representative the measurements made at a particular instant in time are for the overall operations at the plant – which will change as different fuels and raw materials are introduced, and different operating conditions are applied. Estimates based on measurements have been characterised as having greater accuracy for low-level emissions, but lower accuracy for long-term averages, and higher precision, but high associated costs, especially for continuous monitoring systems.

Since the 2005 inventory (AMAP/UNEP, 2008; Pacyna et al., 2009) was produced, the number of direct measurements of emissions from certain point sources (in particular power plants and some metal and cement production and waste incineration facilities) has increased considerably, resulting in a much improved information base.

In a number of countries (including the USA, Canada, Australia, and EU Member States) legal and/or regulatory systems have been introduced that require regular reporting of emissions. Increasing use is being made in these reporting systems of measurement-based estimates and facility-level reporting, in particular for major point sources. A number of these systems support pollution release inventories (PRI) and/or emissions inventories (E-PRTR, 2012; LRTAP, 2012; Environment Canada, 2012; Australian Government, 2012; US EPA, 2012). Some of these systems include an 'emissions threshold' above which plants are required to report their emissions (typically 5 kg/y as for the Canadian NPRI, or 10 kg/y for the European Pollutant Release and Transfer Register, E-PRTR). Different national rules and procedures apply when it comes to checking and auditing the reported facility emissions.

In other countries, national Hg emissions have only recently been quantified for the first time. Since 2005 and the start of the UNEP negotiating process in 2010, many countries have initiated work on national emission inventories which, in several cases, have yielded much improved information on activity data, sector characteristics and Hg emissions. A number of such inventories make use of the 'UNEP Toolkit' for identification and quantification of Hg releases (UNEP 2011a,b) (see Section 2.2.3).

It is important to recognise that all emission estimates, whether national, global, or for an individual plant, and whether based on mass-balance approaches or measurements, are estimates. These estimates rely on the validity of various underlying assumptions. Improving the accuracy of estimates (i.e., reducing their inherent uncertainty) depends on improvements in the quality of the information available to support and better constrain the assumptions.

For the purposes of developing a global inventory of emissions to air, it was beyond the scope of the work to consider emissions at the detailed facility-level, and even incorporation of national estimates is problematic – for reasons discussed in Section 2.3.2. Consequently, for the 2010 inventory, a mass-balance approach was employed with the aim of deriving a complete global inventory using a common approach for all countries (see discussions in Section 2.2.3).

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[3] 'Inventory' in this context means a compilation of the estimated emissions to air from various sectors and sources; there are known source sectors for which it is not (yet) possible to quantify emissions, and possibly also sectors that have not yet been recognized as significant sources of Hg emissions to air.

2.2.2 Previous inventories

The 2008 report (AMAP/UNEP, 2008) included an inventory of anthropogenic Hg emissions to the atmosphere for 2005, which reflected the state-of-the-art at that time. The new (2010) inventory produced for this report, however, represents a radical departure in how data are compiled and used to produce (global) emissions inventories, and includes a comprehensive overhaul of the methodology applied. It is therefore relevant to describe these developments.

Global inventories of Hg emissions to the atmosphere have been produced at approximately five-year intervals since 1990 (Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2009; AMAP/UNEP, 2008). All of these inventories have used the same basic approach for the major (by-product) emission sectors. Namely, for a set of defined emission sectors, national emissions estimates are calculated by multiplying data on the associated **'activity'** (i.e., statistics on consumption of fuels or raw materials used, or amounts of products such as cement or metals produced) by an **'emission factor'** – a value representing the amount of Hg released to the atmosphere per amount of material consumed/produced (Figure 2.2). The emissions factors applied have been **abated emission factors**, that is, emission factors that incorporate the effects of Hg emission controls due to abatement technology, yielding the abated emissions estimates[4].

Figure 2.2. Method used to calculate emissions estimates in previous global inventories.

In the 2005 global inventory prepared in connection with the UNEP 2008 report (AMAP/UNEP, 2008) and the AMAP 2011 Mercury Assessment (AMAP, 2011), an additional component was introduced. This concerned estimating emissions from certain 'intentional-use' sectors not considered in previous global inventories, using a mass-balance approach based on regional Hg consumption patterns. The amounts of Hg entering into waste-streams from disposal of Hg-containing products were modelled, and emission factors applied to calculate associated emissions to air. In addition, estimates were introduced for a major emissions sector associated with use of Hg in ASGM that had not been included in previous global inventories.

Making comparisons between the global inventories prepared since 1990 is problematic for the following reasons:

1. Inventories prepared for different years used different statistical sources for activity data, generally with improvements in completeness of the information in later years; in some cases different procedures and assumptions were made when assigning activity data.
2. Inventories prepared for different years include different combinations of sectors, with additional (intentional use) sectors being added to the 2005 inventory in particular.
3. For many sectors, inventories prepared for different years tended to use the same (abated) emission factors; however, in some cases emission factors were adjusted between the different inventories as better information became available.

As a consequence of this, and in connection with the AMAP assessment (AMAP, 2011) and UNEP Paragraph-29 Study (UNEP, 2010a) the inventories prepared since 1990 were re-calculated in an attempt to gain insight into the effects of the above factors on the implied changes in global anthropogenic Hg emissions over time (AMAP, 2010) (see Section 2.4).

In relation to point (3), the use of the same (abated) emission factors for inventories representing emissions over the period 1990–2005 is, in itself inappropriate. This is because it poorly reflects the reality of the situation where, in particular the technologies applied in processing fuels and raw materials (including technologies to reduce emissions) may have changed significantly over the past 20 years. In cases where adjustments were made, these generally concerned new assumptions regarding the Hg content of fuels and raw materials rather than addressing changes in technology. This issue was not addressed in the re-analysis of past global Hg inventories by AMAP (2010).

2.2.3 New inventory, new methodology

As noted above, one major limitation of the methods employed to produce previous global inventories of anthropogenic Hg emissions to air (including the 2005 inventory) was that these inventories were based on the application of a single (abated) emission factor[5] per sector. That is to say, for any given sector, the same (abated) emission factor (and therefore underlying assumptions) was employed for calculating emissions from all countries, irrespective of the obvious fact that in reality countries differ substantially, both in respect of the fuels and raw materials used and the technologies employed.

This problem is addressed to some degree in the approach adopted in the **UNEP Toolkit** for identification and quantification of Hg releases. The UNEP Toolkit is a series of guidelines and spread-sheet tools developed by UNEP that allow countries to identify and quantify their Hg releases (UNEP, 2011a,b). The Toolkit offers default factors for the calculation of inputs (termed **'input factors'**, which are somewhat comparable to (unabated) emission factors); it also invites countries to introduce an additional factor (an **'output scenario'**) to take into account a basic selection of Hg emission control technologies.

The UNEP Toolkit input factors calculate total Hg releases for the sectors concerned, and emissions to air are determined by the application of an air **'distribution factor'** (i.e., the proportion of

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[4] Abated emissions estimates refer to emissions after the application of control technologies to reduce emissions; unabated emissions refer to emissions prior to the application of these control technologies.

[5] An emission factor reflecting emissions after the application of emission abatement technologies.

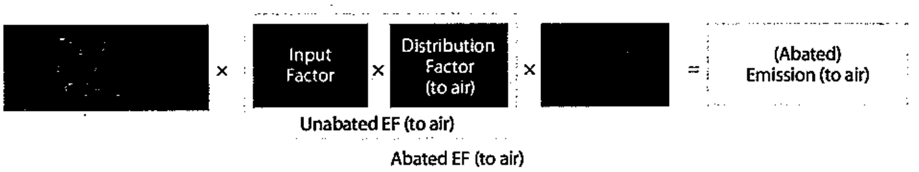

Figure 2.3. Method used to calculate emissions estimates in the UNEP Toolkit approach.

the total release that is assumed to be released to air, as opposed to land or water, etc.). In combination, the UNEP Toolkit **input factor** and **distribution factors** are equivalent to an **unabated emission factor** for the media/pathway concerned (Figure 2.3). Because the UNEP Toolkit is a basic release inventory development tool, it is often used in the 'default mode', with the default input factors and output scenarios being applied. The result is that many of the release estimates produced have a very large associated range (values produced using the minimum and maximum default factors). Most UNEP Toolkit applications employ only a single input factor and output scenario factor, thus the input factor still needs to reflect the proportion of Hg released from the entire mix of fuels and/or raw materials that are used within a given sector in the country, and the output factor the 'aggregated' effect of, for example, any technologies applied to control emissions.

The Toolkit approach does offer the possibility for all countries to use assumptions and specific emission factors that are applicable for their own situation – as opposed to a single uniform set of factors – as applied to previous global inventory estimates. However, producing a global emission inventory using the Toolkit would require that all countries develop and use their own Toolkit application, and all for the same year (or restricted period). To date, the Toolkit has been applied by approximately thirty countries, and for years ranging from 2004 to 2009.

Taking the above into account, it was decided that a new approach was needed for the work to prepare the 2010 global inventory of anthropogenic Hg emissions. The work involved four main components:

1. The development and application of new systems for estimating emissions from main (by-product and some intentional-use) sectors based on a mass-balance approach. This included the development of two database modules, the first to compile and document **activity data**, the second to maintain data on **(unabated) emission factors** and emission reduction technology employed in different countries and to calculate unabated and abated emissions.

   In addition to improved possibilities to take into account differences in fuels and raw materials and the technologies employed in different countries, the new methodology also includes a more detailed breakdown of emissions between different sectors/activities than that employed in previous inventories. An important refinement in this connection is the partitioning of emissions (and the assumptions and factors that are used to calculate them) associated with combustion of fossil fuels in power plants, industrial uses, and other (e.g. domestic/residential burning) (see Section 2.2.4).

   The conceptual approach employed to produce this component of the 2010 inventory is illustrated in Figure 2.4, and can be compared with Figures 2.2 and 2.3 that describe the approaches used in preparing the 1990–2005 global inventories, and the UNEP Toolkit approach.
2. The refinement and application of the (substance-flow) model previously employed (AMAP/UNEP, 2008) to quantify emissions from wastes associated with Hg-containing products (i.e., certain intentional-use sectors), based on regional Hg consumption data.
3. The refinement and application of the model previously employed (AMAP/UNEP, 2008) to quantify emissions from dental amalgam as a result of human cremation.
4. The updating of information on emissions associated with ASGM. Because of the nature of this activity (largely

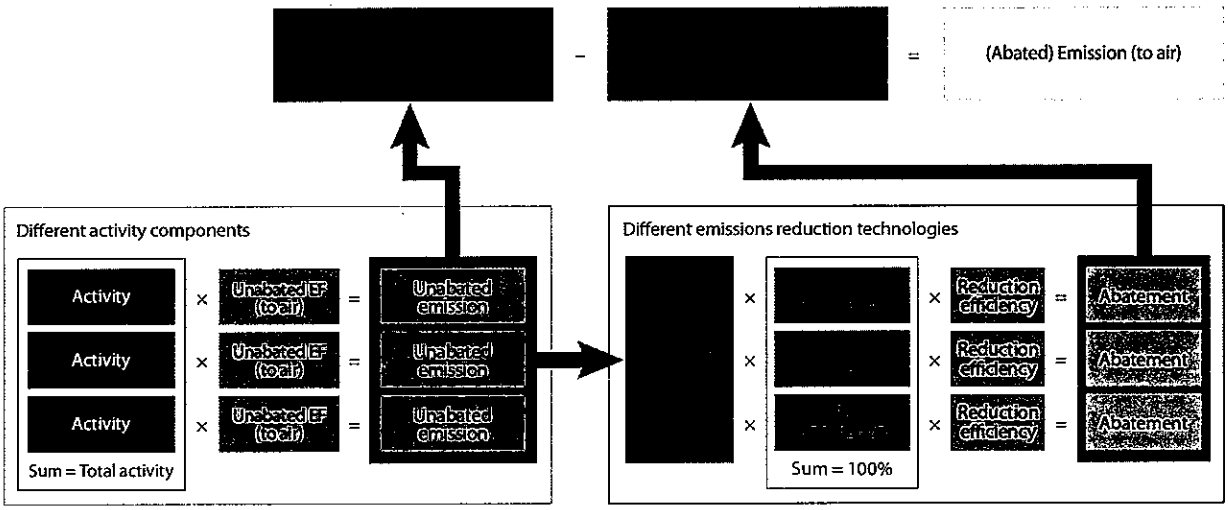

Figure 2.4. Method used to calculate emissions estimates (to air) for the 2010 inventory estimates.

unregulated and illegal in some countries) official data and statistics regarding the extent of ASGM activities are generally lacking or incomplete. For this reason, emissions estimates were prepared by the Artisanal Gold Council, utilising information that is compiled in and accessible through the Mercury Watch website (www.mercurywatch.org). This was the only component of the 2010 inventory that, for some countries, utilised information from earlier than 2008.

A key aspect in developing global emission inventories is transparency in terms of the assumptions made, and the underlying emission factors and activity data utilised in preparing the various inventories. The documentation included in the 2008 technical report (AMAP/UNEP, 2008) was intended to provide more of this information in an accessible form for the 2005 global inventory. However, in view of the ongoing UNEP process to negotiate a global Hg agreement, and the attention this is focusing on Hg emissions, it is increasingly important to be transparent and make accessible comprehensive documentation regarding all the data, assumptions, and calculation methods that constitute the basis for any given emission estimate. The UNEP Toolkit provides transparency in documenting the data that are used to calculate emission estimates; however the decision process behind a country employing a particular input factor or output scenario factor is not always entirely clear. Transparency and documentation of the data and assumptions underlying any given estimates are also critical if future estimates and inventories are to be reliably compared with the 2010 inventory estimates.

For this reason, this chapter includes an extensive set of annexes, with comprehensive discussions of the methods employed to produce estimates for each of the four components described above. These annexes include worked examples and background data relating to activity statistics and emissions factors and technology assumptions used, etc. The relevant Annexes are numbered as follows:

- Annex 1: Method used to estimate 2010 mercury emissions to air from main 'by-product' emission sectors and the chlor-alkali industry, including an example calculation.
- Annex 2: Method used to estimate 2010 mercury emissions to air from artisanal and small-scale gold mining, including an example calculation.
- Annex 3: Method used to estimate 2010 mercury emissions to air from wastes associated with intentional use sectors, including an example calculation.
- Annex 4: Method used to estimate 2010 mercury emissions to air from use in dental amalgam and human cremation.
- Annex 5: Activity data used in the calculation of emission estimates.
- Annex 6: Emission factors and technology profiles used in the calculation of emission estimates.

2.2.3.1 Regionalisation

As previously mentioned, one of the objectives of the new inventory methodology was to overcome the limitation of applying 'universal' (abated) emission factors – that is, the same factors to all countries. In order to better reflect differences in the situations of different countries concerning their technological characteristics and procedures for handling waste, countries were grouped together with other countries believed to have similar technological and/or waste management characteristics. The initial groupings applied were those suggested by Streets et al. (2011), and these groupings were subsequently modified based on expert opinion and information made available to the project group. The resulting country groupings formed the basis for assigning generic technology or waste management profiles that were used in the emissions estimation methodology. In this way, the (already limited) information available for some countries regarding emission factors and technological factors could be used to fill the many gaps in information for other countries in their respective groups. The groupings of countries employed in the estimation of emissions for the main industrial sectors and intentional-use sectors respectively are illustrated in Figures 2.5 and 2.6. The use of these profiles is described in the methodological descriptions in Annexes 1 and 3.

2.2.4 Sectors and activities

2.2.4.1 Sectors and activities quantified in the 2010 inventory

The inventory estimates in the new 2010 global inventory of anthropogenic Hg emissions to air cover the following main emission '**sectors**':

- Stationary combustion of fossil fuels (coal, oil and natural gas) in power plants.
- Stationary combustion of fossil fuels (coal, oil and natural gas) in industrial/commercial uses.
- Stationary combustion of fossil fuels (coal, oil and natural gas) for domestic/residential heating, and uses of coal, (crude, diesel and fuel) oil and gas in transportation, agriculture and fishing.
- Cement manufacture (including co-incineration of waste).
- Production of ferrous metals (primary pig iron production).
- Production of non-ferrous metals (primary production of copper, lead and zinc).
- Production of aluminium[6].
- Production of mercury metal.
- Mercury emissions from oil refining (other than emissions associated with on-site combustion for power/heat)[6].
- Production of gold from large-scale mining.
- Production of gold from artisanal and small-scale gold mining.

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[6] Mercury emissions from production of aluminium and from oil refining have not been included in previous global inventories.

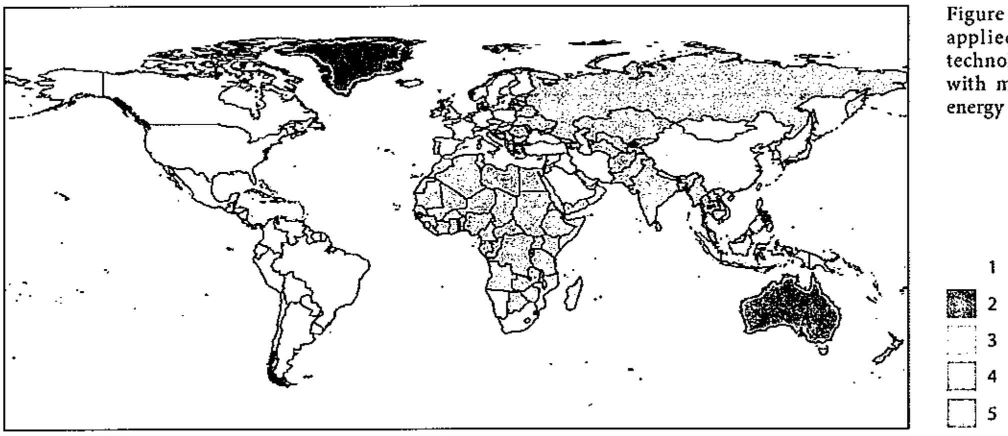

Figure 2.5 Regional groupings applied in the definition of technology profiles associated with mercury emissions from energy and industrial sources.

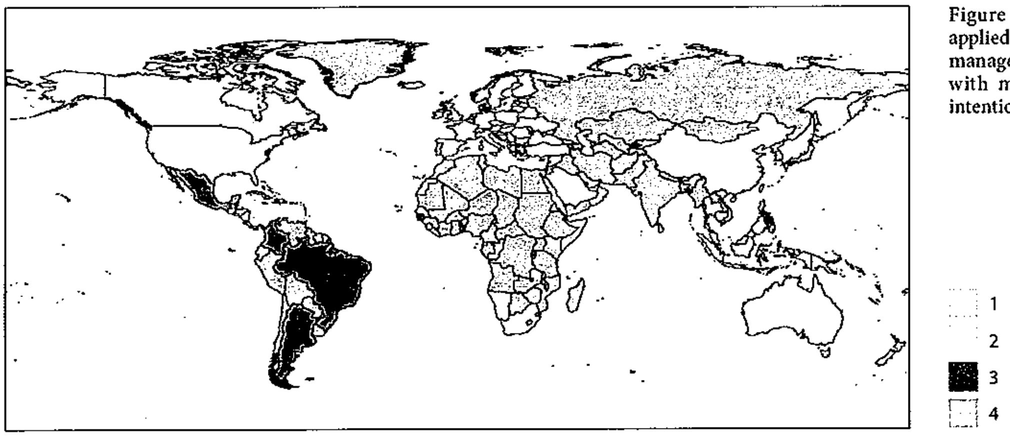

Figure 2.6. Regional groupings applied in the definition of waste management profiles associated with mercury emissions from intentional-use sectors.

- Mercury emissions from chlor-alkali industry (Hg-cell technology).
- Mercury emissions from product waste incineration and other product waste disposal.
- Mercury emissions from its use in dental amalgams resulting from human cremations.

The first ten items are associated with by-product or unintentional Hg releases; the latter four are associated with intentional-uses of Hg (and related waste streams). These emission sectors are essentially the same as those addressed in the 2005 global emissions inventory, with the addition of emissions from aluminium production and oil refineries.

Another new addition to the 2010 inventory is the inclusion of an estimate of emissions from contaminated sites (sites with elevated Hg content relative to local background, as a consequence of Hg use or its presence in a variety of products and industrial processes, such as old mine tailings and industrial sites – including some closed chlor-alkali plants – that are generally no longer operating but that are contaminated as a result of past human activities). Emissions estimates from this source are based on information reported in Kocman et al. (2013).

A further new feature of the 2010 inventory is that several of these sectors, in particular the stationary combustion sectors, have been sub-divided into additional component **'activities'** – so-called because they each have associated **'activity'** data relating to statistics on levels of consumption or production. Thus, for example, in previous inventories, for countries lacking more detailed national inventories, activity data relating to coal and oil consumption were used to estimate emissions – applying a very coarse assumption that 50% was used in power plants and 50% in domestic residential heating. The new methodology compiles activity data not only for power plant, industrial and domestic/residential/transportation fuel burning separately, it also distinguishes between different types of coal and oil consumed. These improvements allow for better characterisation of the fuels in terms of the (unabated) emission factors associated with them. Thus, rather than using a single emission factor for coal burning it is now possible to assign different factors for different types of coal used within a particular country for a particular purpose. The disadvantage of this is, of course, that a more detailed information base needs to be compiled on activity statistics; however such data are increasingly available from national sources, and from international statistical databases such as those compiled by the International Energy Agency (IEA) and the US Geological Survey (USGS) (see Section 2.2.5).

Table 2.1 presents an overview of the relationship between sectors, activities, and also the abbreviations that are used to refer to these various components in the inventory outputs. It also includes information on the relationship between these sectors/activities and the sectors employed for reporting under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP).

Table 2.1. Classification scheme for sectors and their sub-activities employed in the 2010 inventory.

Sector (code)	Component activities (code)	Release category	Relevant LRTAP NFR sector coding(s)[a]
Stationary fossil fuel combustion (SC) in (major) power plants (SC-PP) Coal combustion (SC-PP-coal)	Combustion of hard coal (anthracite) (HC-A-PP) Combustion of hard coal (bituminous coals) (HC-B-PP) Combustion of brown coal (sub-bituminous coals)(BC-S-PP) Combustion of brown coal (lignite)(BC-L-PP)	By-product	1A1a Public electricity and heat production [Sum of emissions from all fuels. Can include waste incinerated for energy recovery.]
Stationary fossil fuel combustion (SC) in (major) power plants (SC-PP) Oil combustion (SC-PP-oil)	Combustion of crude oil (CO-PP) Combustion of heavy fuel oil (CO-HF-PP) Combustion of light fuel oil (CO-LF-PP)	By-product	
Stationary fossil fuel combustion (SC) in (major) power plants (SC-PP) Natural gas combustion (SC-PP-gas)	Combustion of natural gas (NG-PP)	By-product	
Stationary fossil fuel combustion (SC) in industrial uses (SC-IND) Coal combustion (SC-IND-coal)	Combustion of hard coal (HC-IND) Combustion of brown coal/lignite (BC-IND)	By-product	Stationary combustion in manufacturing industries and construction: 1A2a Iron and steel 1A2b Non-ferrous metals 1A2c Chemicals 1A2d Pulp, Paper and Print 1A2e Food processing, beverages and tobacco 1A2fi Other [Sum of emissions from all fuels]
Stationary fossil fuel combustion (SC) in industrial uses (SC-IND) Oil combustion (SC-IND-oil)	Combustion of crude oil (CO-IND) Combustion of heavy fuel oil (CO-HF-IND) Combustion of light fuel oil (CO-LF-IND)	By-product	
Stationary fossil fuel combustion (SC) in industrial uses (SC-IND) Natural gas combustion (SC-IND-gas)	Combustion of natural gas (NG-IND)	By-product	
Stationary fossil fuel combustion (SC) in other uses (domestic/residential uses, transport, and use in fisheries, agriculture) (SC-DR) Coal combustion (SC-DR-coal)	Combustion of hard coal (HC-DR) Combustion of brown coal/lignite (BC-DR)	By-product	1A4ai Commercial / institutional: Stationary; 1A4bi Residential: Stationary plants; 1A4ci Agriculture/Forestry/Fishing: Stationary [Sum of emissions from all fuels]
Stationary fossil fuel combustion (SC) in other uses (domestic/residential uses, transport, and use in fisheries, agriculture) (SC-DR) Oil combustion (SC-DR-oil)	Combustion of crude oil (CO-DR) Combustion of heavy fuel oil (CO-HF-DR) Combustion of light fuel oil (CO-LF-DR)	By-product	
Stationary fossil fuel combustion (SC) in other uses (domestic/residential uses, transport, and use in fisheries, agriculture) (SC-DR) Natural gas combustion (SC-DR-gas)	Combustion of natural gas (NG-DR)	By-product	
Production of iron and steel (PISP)	Primary production of pig iron (PIP)	By-product	2C1 Iron and steel production 1B1b Solid fuel transformation 1B1c Other fugitive emissions from solid fuels 1A2a Iron and steel, stationary combustion [2C1 Includes also secondary steel. 1B1b/c includes coke production Emissions may be classified as process emissions (2C1) and/or emissions from stationary combustion (1A2a) and/or include coke production (1B1b/c).]
Non-ferrous metal production (aluminium, copper, lead and zinc production) (NFMP, NFMP-AL, NFMP-CU, NFMP-PB, NFMP-ZN)	Production of aluminium from bauxite – primary production (AL-P)	By-product	2C3 Aluminium production 1A2b Non-ferrous metals [Includes also secondary aluminium. Emissions may be classified as process emissions (2C3) and/or emissions from stationary combustion (1A2b).]
	Production of refined copper – primary production (CU-P) Production of refined copper – total production (CU-T) (used for some countries where CU-P is not separately quantified)	By-product	2C5a Copper production 2C5e Other metal production 1A2b Non-ferrous metals, stationary combustion [Includes also secondary copper. May be reported included in a sum for all non-ferrous metals in 2C5e. Emissions may be classified as process emissions (2C5a/e) and/or emissions from stationary combustion (1A2b).]

	Production of refined lead – primary production (PB-P) Production of refined lead – total production (PB-T) (used for some countries where PB-P is not separately quantified)	By-product	2C5b Lead production 2C5e Other metal production 1A2b Non-ferrous metals, stationary combustion [Includes also secondary lead. May be reported included in a sum for all non-ferrous metals in 2C5e. Emissions may be classified as process emissions (2C5b/e) and/or emissions from stationary combustion (1A2b).]
	Production of refined zinc – primary production (ZN-P) Production of refined zinc – total production (ZN-T) (used for some countries where ZN-P is not separately quantified)	By-product	2C5d Zinc production 2C5e Other metal production 1A2b Non-ferrous metals, stationary combustion [Includes also secondary zinc. May be reported included in a sum for all non-ferrous metals in 2C5e. Emissions may be classified as process emissions (2C5d/e) and/or emissions from stationary combustion (1A2b).]
Non-ferrous metal production (mercury) (NFMP-HG)	Production of Hg (primary sources) (HG-P)	By-product	2C5e Other metal production 1A2b Non-ferrous metals [May be included in a sum for all non-ferrous metals in 2C5e. Emissions may be classified as process emissions (2C5e) and/or emissions from stationary combustion (1A2b).]
Non-ferrous metal production: Large-scale gold production (NFMP-AU)	Production of gold from large-scale mining (GP-L)	By-product	2C5e Other metal production 1A2b Non-ferrous metals, stationary combustion [May be included in a sum for all non-ferrous metals in 2C5e. Emissions may be classified as process emissions (2C5e) and/or emissions from stationary combustion (1A2b).]
Artisanal and small-scale gold production (ASGM)	Production of gold (artisanal /small-scale) (GP-A)	Intentional use	2C5e Other metal production [May include emissions from all/other nonferrous metals production.]
Cement production (CEM)	Production of Portland cement (CEM)	By-product	2 A 1 Cement production 1 A 2 f i Other stationary combustion [Emissions may be classified as process emissions (2 A 1) and/or emissions from stationary combustion (1 A 2 f i).]
Caustic soda production (CSP)	Chlor-alkali industry using Hg-cell process, based on plant Cl_2 production capacity (CSP-C) or Cl_2 production amount (CSP-P)	Intentional use	2B5a Other chemical industry [Includes all other chemical industries except ammonia production, nitric acid production, adipic acid production and carbide production.]
Oil refining (OR)	Refining of crude oil in oil refineries (CO-OR)	By-product	1A1b Petroleum refining 1B2ai Exploration, production, transport 1B2aiv Refining / storage 1B2c Venting and flaring [May include venting/flaring of natural gas]
Dental use (DENT)	Use in dental amalgam, emissions from human cremation (CREM)	Intentional use	6Cd Cremation
Waste (WAS)	Incineration of waste (large incinerators) (WI)	Intentional use	6Cc Municipal waste incineration [6Cc may include uncontrolled waste incineration. Waste incinerated for energy recovery may be included in 1A1a Waste incineration, irrespective of origin may be reported as a sum under one of the 6C categories]
	Waste and other losses due to breakage and disposal in landfill, etc. (WASOTH) [Industrial waste incineration and incineration of sewage sludge are not included in the 2010 emissions estimates.]	Intentional use	3D3 Other product use 6Ca Clinical waste incineration (6Cb Industrial waste incineration) 6Ce Small scale waste burning 6D Other waste
Contaminated Sites (CSITE)	Contaminated sites associated with no longer operational mining activities and closed industrial plants (CSITE)	Past use	?

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[a] Reporting of emissions under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) is done using a specified format (NFR-reporting templates) (www.ceip.at/reporting-instructions/annexes-to-the-reporting-guidelines). When comparing emissions from sectors, in the reporting tables Parties have the possibility to make their own choices to aggregate emissions from several sources and report a notation key IE (included elsewhere) if this is clearly explained in the accompanying Inventory report.

2.2.4.2 Sectors and activities not quantified in the 2010 inventory

In addition to identifying the sectors that are included in the 2010 global inventory calculations, it is important also to identify the (potentially relevant) sectors and activities that are not (yet) addressed or fully quantified in the inventory. These include:

- Secondary metal production[7]
- Production of manganese and/or manganese alloys (e.g., ferro- manganese alloys)
- VCM production with Hg-dichloride catalyst
- Other manufacturing processes (pulp and paper manufacture, brewing and distilling, etc.)
- Emissions associated with incineration of sewage sludge
- Emissions associated with industrial waste (including incineration of industrial waste)
- Extraction of petroleum hydrocarbons (i.e., Hg emissions prior to refining/combustion of oil, from gas flaring, and prior to transport and combustion of gas)
- Releases from dental use during production and preparation of Hg amalgam fillings, and disposal of removed fillings
- Emissions associated with biofuel production and burning in power plants and industrial sectors
- Other anthropogenic biomass burning.

Emissions associated with some of these additional activities are quantified in national inventory compilations, and where these are compared with or introduced into the global inventory they are separately identified (see Annex 7).

2.2.5 Sources of data and information used in the 2010 inventory

Primary sources of data and information used in the production of the 2010 global emissions inventory are described in Table 2.2. In addition, comprehensive national data were provided, especially for Brazil, Japan, Republic of Korea, Mexico, and the USA, much of this through the members of the UNEP/AMAP contact group established to support the work to produce an updated 2010 global inventory of anthropogenic Hg emissions to air.

A large number of additional information and data sources were used as the basis for the work to determine (unabated) emission factors and 'technology profiles', in particular for country-specific emission factors and technology characterisations. These, together with comprehensive descriptions of the procedures employed are detailed in Annex 6.

2.2.6 Relationship with the UNEP Toolkit

The databases compiled to support the current inventory work made use of the UNEP Toolkit (UNEP, 2011b) as a basis for development of in particular (unabated) emission factors (see Annex 6). In the course of this work, many of the Toolkit factors were adapted for the activity data concerned, or adjusted on the basis of additional information available from, for example, the Paragraph-29 study work (UNEP, 2010a), or from national and industry sources. As a result of this work, a parallel activity has been initiated by UNEP to update the UNEP Toolkit documentation.

Some points to note when comparing the UNEP Toolkit with the database approach adopted in this work:

- The databases are constructed to prepare global emission estimates, that is, estimates for all countries; whereas the Toolkit is designed for use on a country by country basis. The database is applied to all countries, for a single target year whereas the Toolkit applications (to date) are for a range of different years.
- The Toolkit produces estimates of releases to air, water and land, whereas the databases are (currently) only set up to estimate emissions to air.
- The activity statistics employed in the UNEP Toolkit are not always (readily) available at a global level. For example, the Toolkit calculates emissions from cement production on the basis of clinker production, which simplifies some of the underlying assumptions regarding the processes and sources of Hg involved. However, available (global) production statistics are for cement production, and not for clinker production. Consequently, the database represents a compromise between an ideal approach and one that is applicable for all countries.

Considering the results of Toolkit applications to date, agreement between Toolkit estimates and those produced in this work is variable. In part this reflects the differences in activity data (as many Toolkit applications are for years earlier than 2010). Also, the emission factors employed in the current work, although often based on the published Toolkit factors, have been revised for a number of sectors.

In general, and particularly once ongoing work to update the Toolkit has been completed, the databases developed to prepare global estimates can be expected to produce comparable – but not necessarily identical – results for emissions to air to those produced using the UNEP Toolkit. The databases may be expected to produce improved estimates for some countries where available national information can extend the options available in the Toolkit.

2.2.6.1 Potential future uses of the inventory databases

Optionally, the databases produced to prepare the 2010 global inventory could be employed in a 'Toolkit mode' – introducing the Toolkit default (or modified) emission factors and activity

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[7] Mercury emissions from secondary production of ferrous and non-ferrous metals are not included in the 2010 global inventory estimates as they were assumed to be minor in comparison to emissions associated with primary production. However, this may not be the case in some countries and this issue is discussed further in Section 2.3.3.3. Emissions associated with secondary steel production (which have been quantified in previous inventories) are now included in the re-cycling component of the estimates associated with wastes from intentional use sectors.

Table 2.2. Primary sources of activity and other related data used.

Sector	Activity data[a]	Unabated emission factors[b]	Technology[b]	Other
Coal burning in power plants, industrial and domestic / residential / transport applications	IEA-SB[c]	UNEP, 2010a,b, 2011b,c,d; BREF, 2006	UNEP, 2010a,b, 2011b,c,d; BREF, 2006	
Oil burning in power plants, industrial and domestic / residential / transport applications	IEA-SB[c]	UNEP, 2011b; BREF, 2006	UNEP, 2011b; BREF, 2006	
Natural gas burning in power plants, industrial and domestic / residential / transport applications	IEA-SB[c]	UNEP, 2011b	UNEP, 2011b	
Cement production	USGS, 2009/2010	UNEP, 2010a, 2011b; BREF, 2010	UNEP, 2010a, 2011b; BREF, 2010	CSI, 2005 (waste co-incineration); CEMBUREAU, 2010
Ferrous metal (pig iron) production	Worldsteel Association, 2011	UNEP, 2011b; BREF, 2012a	UNEP, 2011b; BREF, 2012a	
Non-ferrous metal (Cu, Pb, Zn) production	USGS, 2009/2010	UNEP, 2010a, 2011b; BREF, 2009	UNEP, 2010a, 2011b; BREF, 2009	
Aluminium production	USGS, 2009/2010	UNEP, 2011b		
Mercury production	USGS, 2009/2010	UNEP, 2011b		
Large-scale gold production	USGS, 2009/2010	UNEP, 2011b		
Artisanal and small-scale gold production	Artisanal Gold Council	Artisanal Gold Council/ UNEP Partnership on Reducing Mercury in Artisanal and Small-scale Gold Mining	Artisanal Gold Council/ UNEP Partnership on Reducing Mercury in Artisanal and Small-scale Gold Mining	
Chlor-alkali industry	UNEP/World Chlorine Council	UNEP, 2011b		OSPAR, 2011
Oil refining	IEA-SB	UNEP, 2011b; BREF, 2012b	BREF, 2012b	Wilhelm et al., 2007; IKIMP, 2012; IPIECA, 2012; Petroleum Association of Japan
Intentional-use sector emissions (and associated releases from waste incineration / disposal)	P. Maxson, pers. comm.			
Cremation (emissions from dental amalgam)	CSGB, various dates	UNEP, 2011b		
Contaminated sites				Kocman et al., 2013

[a] See Annex 5; [b] See Annex 6; [c] IEA categories – SC-PP: Electricity plants, CHP plants, Heat plants, Energy industry own use; SC-IND: Industry; SC-DR: Transport, Residential, Commercial and Public Services, Agriculture/Forestry, Fishing, Other non-specified.

data – and potentially used to maintain Toolkit results over a longer period of time. The databases could also be readily extended to cover releases to land and water.

The database results can also be used to give insight into possible necessary adjustments that may be needed to the Toolkit default factors, to keep these up to date.

Bearing in mind the difficulties in comparing inventories produced at different times, it may be feasible at some point to use the compiled databases to simulate the approach used to produce past global inventories – out of academic interest. In this connection, however, the new methodology is considered to represent a significant improvement over approaches used in the past. The databases compiled could be considered a starting point for a more organised structured approach to compiling and documenting the data and methods behind the calculations of global emissions inventories – and thus a strategy designed to make these more comparable in the future.

Finally, the databases compiled to support the current inventory work also make it possible to better attempt to establish emissions scenarios – for example by changing assumptions relating to (unabated) emission factors (e.g., resulting from changes in fuel sources and/or raw materials) or changing the technology profiles for various countries/ sectors in a meaningful manner.

2.2.7 Uncertainties

Estimating the uncertainties associated with emission estimates; in particular estimates covered by the scope of a global inventory is a particular challenge. It was beyond the scope of the current project work to investigate this aspect in detail; therefore a relatively crude (and intentionally conservative) approach was adopted to provide some quantification of the scale of uncertainties in the estimates presented.

Uncertainties associated with the emission estimates presented in this report are considered to have three major components:

- uncertainties associated with activity data
- uncertainties associated with (unabated) emission factors
- uncertainties associated with assumptions made regarding applied (Hg emissions control) technologies.

In general, the uncertainties associated with emission factors (including plant operating conditions and technologies used to reduce Hg emissions) are assumed to be considerably more important in determining uncertainties in the overall emissions estimates than those associated with activity data. For example, the EMEP/EEA (2009) air pollutant emission inventory guidebook assigns uncertainties associated with activity data (not specific to Hg) of the order of ± 5–10%. Evaluation of uncertainties associated with (emission factor-based) estimates depends on the procedures involved. For estimates based on a small number of measurements at representative facilities (or engineering judgment based on relevant facts) or engineering calculations based on assumptions alone – which between them cover the case for most Hg emissions estimates – the uncertainties are considered to be of the order of ± 50% to ± an order of magnitude.

In order to provide some quantification of the uncertainties associated with the 2010 global inventory, upper and lower range emissions estimates for major emission sectors were calculated by applying the emissions calculation methodology (as described above) but using adjustments to key information components as described in Table 2.3.

For emissions based on Hg consumption in intentional-use sectors, and associated waste handling, upper and lower range estimates were produced using the respective upper and lower ranges of the Hg consumption data. These however do not reflect the considerable uncertainties associated with the assumptions made regarding Hg flow in waste streams and associated emission factors. Consequently uncertainties in estimates associated with these sectors were assigned at ± a factor of 3.

Uncertainties associated with the assumptions regarding assignment of countries to particular 'country groupings' for applied technology or waste handling procedures were not taken into account.

Table 2.3. Procedures adopted for calculating low/high range emissions estimates.

Category	Lower range estimate	Upper range estimate	Source
Activity data derived from IEA / official national sources - OECD countries	Activity – 5%	Activity + 5%	Modified after EMEP/EEA, 2009
Activity data derived from IEA / official national sources – non-OECD countries	Activity – 10%	Activity + 10%	Modified after EMEP/EEA, 2009
Activity data derived from other sources	Activity – 30%	Activity + 30%	Based on AMAP/UNEP, 2008
Unabated emission factors (UEFs)	If lower UEF available, mid-range UEF[a] – 0.5 × the difference between the lower and mid-range UEF. Otherwise, 0.7 × UEF[a] for coal sectors; 0.01 × UEF[a] for large scale gold production; 0.5 × UEF[a] for all other sectors	If upper UEF available, mid-range UEF[a] + 0.5 × the difference between the mid- and upper-range UEF. Otherwise, 1.3 × UEF[a] for coal sectors; 1.99 × UEF[a] for large-scale gold production; 1.5 × UEF[a] for all other sectors	UEFs tabulated in Annex 6
Technology profile	Uncertainties associated with the applied assumptions regarding abatement technology were not introduced directly into the calculations. In connection with these assumptions, the assumptions concerning types of controls and degree of implementation are considered to be more critical than those concerning Hg emission reduction effectiveness. To partly account for this, uncertainties associated with UEFs were somewhat increased.		
Emissions estimates for intentional-use waste stream emissions and emissions from cremations	0.3 × Mid-range estimate	3 × Mid-range estimate	
Emissions estimates for ASGM	Mid-range estimate –30–75% depending on country	Mid-range estimate + 30–75% depending on country	

[a] UEF as tabulated in Annex 6

For emissions associated with ASGM, low–high range estimates were derived based on assumed Hg use and evaluation of the quality of the available information base for the various countries.

The resulting upper and lower range emission estimates are reported together with the 2010 global inventory estimates presented in Annex 8.

The uncertainties implied by the upper and lower ranges assigned to the presented estimates are somewhat larger than those reported with some previous inventories. This may be counter-intuitive given the presumption of improvements in both the methodologies and information base on which the estimates are founded. However, it is a reflection of the conservative assumptions employed, and the fact that previous assessments of uncertainties may have been over-optimistic, in particular with regard to the major influence of relatively small adjustments to emission factors.

Very few countries quantify uncertainties in relation to their national emissions reporting. However, for comparative purposes, the uncertainties estimated by Finland in their report on (2009) Hg emissions to air prepared in connection with their reporting under the LRTAP Convention (SYKE, 2012) is included in Table 2.4.

2.2.7.1 Possible double counting issues

In the production of global inventories based on available activity statistics and emission factors derived from various sources, there is always a potential for double counting. For example, emission factors associated with industrial processes may or may not include fuels used in various parts of the process. By better distinguishing categories of fuel combustion, and by separately addressing unabated emissions and technologies associated with Hg control (abatement) technologies, efforts have been made to avoid potential double counting of emissions. More information on this aspect of the work can be found in Annex 6 where details of the emission factors and technology profiles used in the calculation of emission estimates are discussed.

2.2.7.2 Potential for underestimation

In addition to the uncertainties associated with specific estimates that have been made, the overall inventory total is also a reflection of the completeness of the sources for which estimates have been made. A number of sectors are identified above (Section 2.2.4) that are not included in the current inventory, and that may have significant associated emissions. Some of these sectors are further considered in the discussions below.

Table 2.4. Uncertainties assigned to Finnish (2009) national emissions reported to LRTAP.

EMEP/ NFR sector	Sector description	Uncertainty-lower, %[a]	Uncertainty-upper, %[a]
	Energy Industries		
1A1a	Public Electricity and Heat Production	-35	33
1A1b	Petroleum refining	-80	80
	Manufacturing Industries and Construction		
1A2a	Iron and Steel	-80	80
1A2b	Non-ferrous metals	-90	89
1A2c	Chemicals	-47	47
1A2d	Pulp, paper and print	-53	54
1A2e	Food-processing, beverages and tobacco	-73	72
1A2fi	Other	-45	45
	Transport		
1A3bvi	Automobile tyre and break wear	-98	239
	Other sectors		
1A4ai	Commercial institutional	-67	65
1A4bi	Residential plants	-84	85
1A4ci	Agriculture, forestry, fishing (stationary)	-55	56
1A5A	Other stationary (including military)	-68	66
	Mineral Products		
2A1	Cement production	-50	50
2A2	Lime production	-100	101
	Chemical Industry		
2B5a	Other	-52	51
	Metal production		
2C1	Iron and steel production	-49	48
2C2	Ferroalloys production	-51	50
2C5d	Other	-100	98
	Other		
2G	–	-100	100
3D3	–	-98	251
	Waste Disposal		
6A	Waste disposal on land	-100	100
6Cb	Waste incineration	-42	43
6Cc	Waste incineration	-37	38
6Cd	Waste incineration	-95	249
Total		-22	22

[a] Expressed as upper and lower bounds of 95% confidence interval relative to mean value.

2.3 Estimating global anthropogenic mercury emissions to air for 2008–2010: Results

Using the methods described above, the total estimated inventory of current (2010) anthropogenic Hg emissions to air is 1960 (1010–4070) t/y.

A complete listing of national emissions estimates obtained using the procedures described above, for various activity sectors, and including low and high range estimates is presented in Annex 8. These tabulations also include, where available comparative estimates from national sources. In light of an ongoing re-evaluation of default factors employed in the UNEP Toolkit, which is taking account of information acquired during the preparation of the 2010 inventory, estimates made using past applications of the UNEP Toolkit were not considered appropriate in most cases as most of these applications employed Toolkit default factors.

For some countries, comprehensive national emissions inventories for the period 2008–2010 are available (see Annex 7 and Section 2.3.2). Where such national inventories have an appropriate degree of documentation and transparency with regard to the basis for the estimates, these national estimates are suitable for use in the global inventory. In such cases they can be used to replace the estimates produced using the generic global inventory procedures – reflecting the fact that the information available to national authorities forming the basis for the estimates (national activity data, emissions measurements at facilities, etc.) should be better than that available from (global) statistical compendia, literature reviews and associated assumptions, etc.

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

2.3.1 Inventory results by region and sector

On the basis of the inventory presented in Annex 8, Table 2.5 summarises the distribution of the estimates of global anthropogenic Hg emissions to air in 2010 according to sub-continental regions[8].

Table 2.6 presents the results per region on a per capita basis, for ASGM and other sectors and their combination. Note here that the ASGM emissions are per capita for the entire regional population and not just for that part of the population engaged in ASGM activities.

Table 2.5. Global anthropogenic mercury emissions to air from different regions in 2010. IMPORTANT: These numbers cannot be compared directly with those presented in the 2008 assessment; see Section 2.4.

Sub-continent	2010 emissions (range), t[a]	%
Australia, New Zealand & Oceania	22.3 (5.4 – 52.7)	1.1
Central America and the Caribbean	47.2 (19.7 – 97.4)	2.4
CIS & other European countries	115 (42.6 – 289)	5.9
East and Southeast Asia	777 (395 – 1690)	39.7
European Union	87.5 (44.5 – 226)	4.5
Middle Eastern States	37.0 (16.1 – 106)	1.9
North Africa	13.6 (4.8 – 41.2)	0.7
North America	60.7 (34.3 – 139)	3.1
South America	245 (128 – 465)	12.5
South Asia	154 (78.2 – 358)	7.9
Sub-Saharan Africa	316 (168 – 514)	16.1
Region undefined[b]	82.5 (70.0 – 95.0)	4.2
Total	1960 (1010 – 4070)	100

[a] Values rounded to three significant figures; [b] emissions from contaminated sites.

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[8] Note: for a definition of these sub-continental regions see Figure 2.8; the sub-continental regions employed in this breakdown have no relationship to the 'regionalisation' employed in the definition of technology and waste profiles (Section 2.2.3.1). Assignment of countries to the sub-continental regions identified in Table 2.5 can be found in Annex 8.

Table 2.6. Per capita anthropogenic mercury emissions to air in different regions in 2010.

Sub-continent	Per capita emissions, g	Per capita emissions from ASGM, g	Per capita emissions from other sectors, g
Australia, New Zealand & Oceania	0.79	0.00	0.79
Central America and the Caribbean	0.26	0.13	0.13
CIS & other European countries	0.34	0.04	0.30
East and Southeast Asia	0.37	0.13	0.24
European Union	0.19	0.00	0.19
Middle Eastern States	0.14	0.00	0.14
North Africa	0.08	0.00	0.08
North America	0.18	0.00	0.18
South America	0.65	0.49	0.16
South Asia	0.10	0.00	0.10
Sub-Saharan Africa	0.39	0.29	0.10
Global	0.28	0.11	0.17

Figure 2.7 and Table 2.7 summarise the distribution of the estimates of global anthropogenic Hg emissions to air in 2010 according to sector.

The majority of global anthropogenic emissions of Hg to the atmosphere in 2010 are associated with ASGM (37%) and stationary combustion of fossil fuels (24.7%, 24.2% from coal combustion). Other major emission sectors include non-ferrous metal production (15.5%, including copper, lead, zinc, aluminium, Hg, and large-scale gold production) and cement production (8.8%).

These results are generally consistent with the sector breakdown presented for the 2005 global inventory (UNEP Chemicals Branch, 2008) with one significant difference. In the 2005 inventory, emissions associated with fossil fuel combustion and ASGM were quantified at ca. 878 t and 350 t, respectively, corresponding to 45.6% and 18.2% of total emissions. In the 2010 inventory, in percentage terms, ASGM accounts for a higher proportion of emissions (37%) than coal combustion (ca. 25%). However, this should not be interpreted as a 'real' trend in terms of large increases in emissions from ASGM between 2005 and 2010, and large decreases in emissions from fossil fuel combustion over the same period. As described below (see Section 2.4.4), much of the apparent increase in ASGM associated emissions is attributed to improved information on ASGM activities in certain regions, and related new estimation methods. As far as the apparent change in emissions from coal burning is concerned, this has two contributing components:

1. In the power generation and industry sectors, new information on coal Hg content has resulted in a lowering of the emissions factors. In the 2005 inventory, abated emission factors of 0.1–0.3 g/t coal were employed. In the 2010 inventory, unabated emission factors combined with information and assumptions regarding efficiency of Hg emission controls at these point sources resulted in (global average) effective abated emission factors (that is global emissions divided by global activity numbers for the sector concerned) of ca. 0.07 g/t for coal burned in power plants and 0.13 g/t for coal burned in industrial sectors. In terms of tonnes of emissions, if the 2010 methodology is applied to the 2005 coal consumption data (see Section 2.4.3) the resulting revised emission estimate for 2005 (ca. 460 t) is about 20% lower than that published in the AMAP/UNEP (2008) report for coal burning in power plants. This reflects the lower

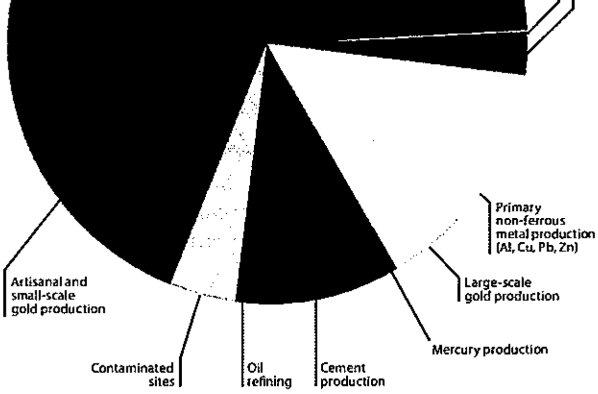

Figure 2.7. Proportions of global anthropogenic mercury emissions to air in 2010 from different sectors.

Table 2.7. Global anthropogenic mercury emissions to air from different sectors in 2010. IMPORTANT: These numbers cannot be compared directly with those presented in the 2008 assessment; see Section 2.4.

Sector	2010 emission (range), t[a]	%
Artisanal and small-scale gold mining	727 (410 – 1040)	37.1
Coal combustion – power plants	316 (204 – 452)	16.1
Coal combustion – industry	102 (64.7 – 146)	5.2
Coal combustion – other	56.0 (35.4 – 80.0)	2.9
Oil combustion – power plants	3.7 (1.7 – 6.1)	0.2
Oil combustion – industry	3.0 (1.4 – 5.0)	0.2
Oil combustion – other	2.6 (1.2 – 4.2)	0.1
Natural gas combustion – power plants	0.3 (0.1 – 0.5)	0.0
Natural gas combustion – industry	0.1 (0.0 – 0.2)	0.0
Natural gas combustion – other	0.2 (0.1 – 0.3)	0.0
Pig iron production (primary)	45.5 (20.5 – 241)	2.3
Non-ferrous metal production		
(Al, Cu, Pb, Zn)(primary)	194 (82.0 – 660)	9.9
Large-scale gold production	97.3 (0.7 – 247)	5.0
Mercury production	11.7 (6.9 – 17.8)	0.6
Cement production	173 (65.5 – 646)	8.8
Chlor-alkali industry (Hg cell)	28.4 (10.2 – 54.7)	1.4
Oil refining	16.0 (7.3 – 26.4)	0.8
Waste from consumer products (landfill)	89.4 (22.2 – 308)	4.6
Waste from consumer products (controlled incineration)	6.2 (1.5 – 21.9)	0.3
Cremation	3.6 (0.9 – 11.9)	0.2
Contaminated sites	82.5 (70.0 – 95.0)	4.2

[a] Values rounded to three significant figures.

emission factors used. The fact that the revised 2005 estimate (410 t) is very similar to the 2010 estimate of ca. 420 t (for the comparable sectors) supports the conclusion that increasing global coal consumption in power and industrial sectors is being offset by improvements in power plant generating efficiency and wider introduction of Hg emissions control.

2. In the 'other' coal-use sector (much of which is associated with domestic and residential coal burning) the story is somewhat different. In 2005, an emission factor of 0.3 g/t was applied to this activity. In addition, since activity data on coal consumption broken down between various sub-sectors was not available for most countries, an assumption was made that ca. 50% was burned in the power/industry sectors and 50% in domestic/residential coal burning. In this case, Hg abatement is not a major consideration. Estimated emissions in 2010 (ca. 56 t) are considerably lower than those reported in the 2005 inventory (375 t) partly due to the use of a lower emission factor, but mainly due to the lower activity data obtained through reported consumption in this sector as opposed to an assumed 50% of total coal consumption. Using the 2010 methodology on 2005 activity and assuming that total coal consumption in 2005 is divided between power, industry and other uses in similar proportions to that in 2010, a revised 2005 emission estimate of ca. 50 t from this sector is obtained. On this basis it could be concluded that emissions from domestic and residential coal burning were over-estimated in the 2005 inventory.

The 2005–2010 comparisons are further discussed in Section 2.4.

Figure 2.8 presents the 2010 inventory results graphically by region and sector. In this illustration, the emissions associated with ASGM are shown separately (so that distributions can be compared more readily between regions with and without ASGM); ASGM symbols are scaled to match those representing emissions from other sectors. The illustration clearly depicts the relative contribution of East and Southeast Asia to global anthropogenic Hg emissions to air, and of some regions in the southern hemisphere to emissions from ASGM.

2.3.2 Comparison of estimates with national reported inventories

During the course of the work to prepare the 2010 inventory, several countries provided comprehensive national emission estimates for years between 2008 and 2010 (Canada, Denmark, Finland, France, Japan, Republic of Korea, Mexico, Norway, Sweden, USA). Other countries (Argentina, Brazil, South Africa) provided comparable information for certain sectors. Additional national estimates are also available from national pollution release inventories and other regional systems (such as reporting under the LRTAP Convention (LRTAP, 2012), and OSPAR Convention reporting of chlor-alkali industry emissions in the OSPAR area (OSPAR, 2011)).

In preparing the 2010 global inventory, an approach was used whereby emissions estimates were produced for all countries using a common methodology, with transparent access to the data and assumptions used to obtain the various estimates. This approach was intentionally designed to ensure a common basis for comparisons. As such, the resulting inventory and methods employed are not 'tuned' for producing the most accurate estimates for any given country or sector. At the same time, detailed national information is critical, both for constraining assumptions and establishing factors that could be applied to other countries with similar situations but lacking their own inventories.

An important test of the validity of the methodology therefore involved comparison of derived inventory estimates with reported national estimates, or estimates produced using other approaches. This was done in an iterative manner, so that where discrepancies were identified, discussions were held to try to understand the reasons for these. Where appropriate,

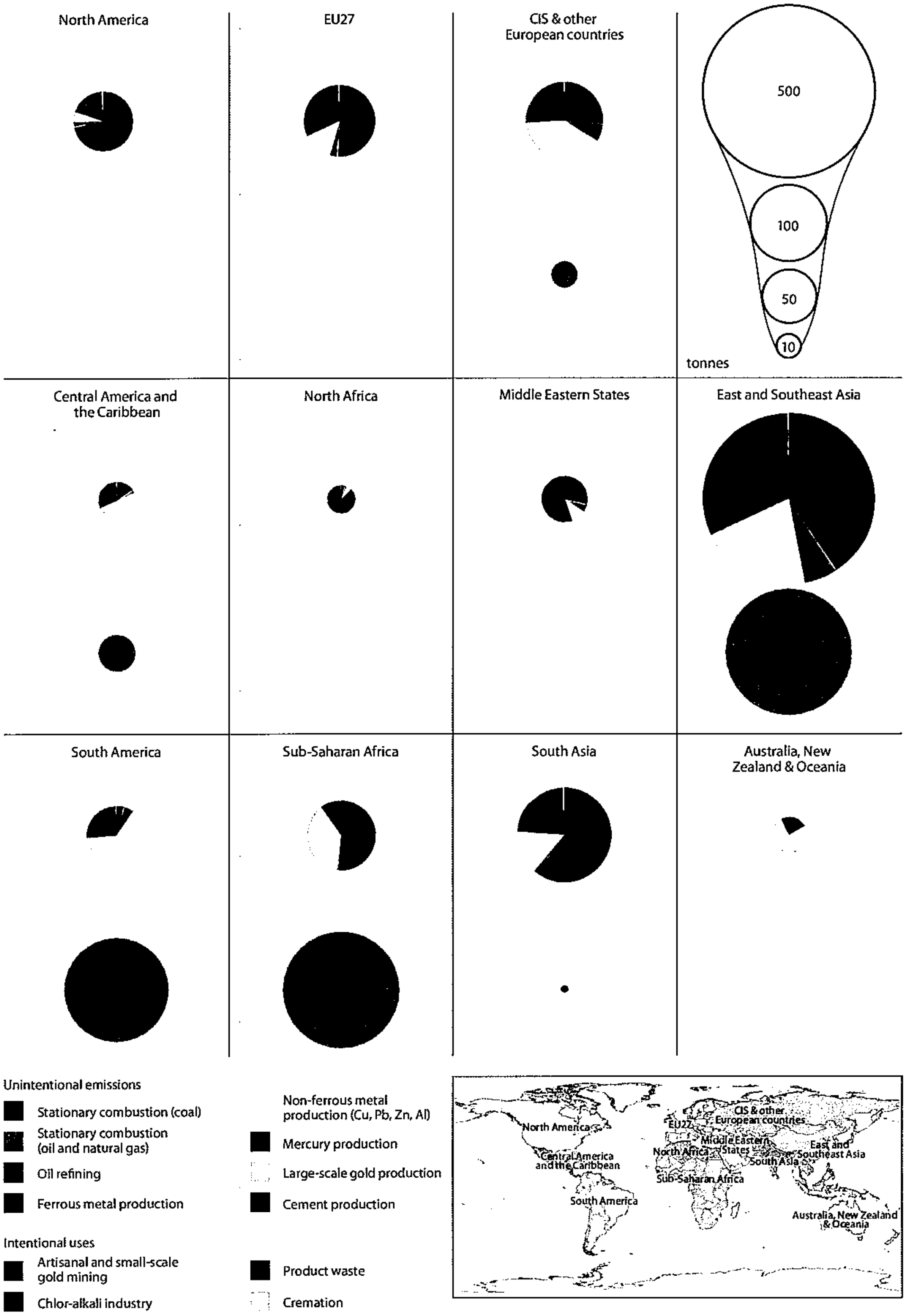

Figure 2.8. Regional pattern of global anthropogenic mercury emissions to air in 2010 from different sectors (does not include emissions from contaminated sites).

Table 2.8. Comparison of 2010 inventory derived estimates with nationally reported estimates for 2010 (USA for 2008).

Country	Estimate obtained from the 2010 global inventory, t	Reported total national emissions, t	Reported national emissions (national reporting) – comparable sectors[a], t	Reported national emissions (national reporting) – other sectors, t	Reported national estimate from LRTAP reporting – comparable sectors[a], t
Australia (and Christmas Island)	21.346	21.604	8.152	13.452	
Austria	0.889	0.986			0.984
Belgium	1.950	2.052			1.757
Bulgaria	8.146	0.884			0.866
Canada	4.470	5.450	4.023	1.427	
Cyprus	0.206	0.127			0.127
Czech Republic	4.896	3.480			3.458
Denmark	0.507	0.440			0.413
Estonia	0.874	0.632			0.632
Finland	1.515	0.898			0.828
France	4.926	4.177			3.225
Germany	17.730	9.292			9.020
Greece	6.513	6.513			
Hungary	1.455	0.781			0.689
Ireland	0.438	0.424			0.402
Italy	4.598	9.520			9.115
Japan	17.228	19.624	17.790	1.834	
Korea- Republic of	7.223	8.039	8.039		
Latvia	0.044	0.076			0.075
Lithuania	0.120	0.387			0.387
Malta	0.014	0.011			0.007
Mexico	23.392	20.519	20.142	0.377	
Netherlands	1.803	0.686			0.673
Norway	0.670	0.580			0.452
Poland	11.758	14.846			14.358
Portugal	0.981	2.055			2.038
Romania	5.027	5.337			5.292
Slovakia	0.950	1.184			0.860
Slovenia	0.497	0.661			0.652
Spain	5.980	7.818			7.454
Sweden	0.772	0.554			0.510
Switzerland	0.533	1.054			0.939
United Kingdom	4.820	6.291			4.642
United States	56.262	55.597	44.686	10.911	

[a] 'comparable sectors' are intended to relate to sectors quantified in the 2010 global inventory. The LRTAP/NFR sectors included in this grouping are as follows: 1A1a, 1A1c, 1A2a, 1A2b, 1A2c, 1A2d, 1A2e, 1A2fi, 1A2fii, 1A3biii, 1A3c, 1A3di(ii), 1A3dii, 1A4ai, 1A4bi, 1A4bii, 1A4cI, 1A4cii, 1A4ciii, 1A5a, 2C1, 2C3, 2C5a, 2C5b, 2C5d, 2C5e, 2A1, 1A1b, 1B2aiv, 6Cd, 6Cc, 6Ce, 3D3, 6D.

Note: Precise alignment of sectors used in different reporting systems is not straightforward and the categorisations in the table above are made employing a basic interpretation of sector descriptions.

Reported national estimate from LRTAP reporting – other sectors, t	Reported emissions from the European Pollutant Release and Transfer Register, t	Source
		Australian Government, 2012
0.002	0.092	LRTAP, 2012; E-PRTR, 2012
0.295	0.979	LRTAP, 2012; E-PRTR, 2012
0.018	0.000	LRTAP, 2012; E-PRTR, 2012
		Environment Canada, 2012
0	0.115	LRTAP, 2012; E-PRTR, 2012
0.023	2.968	LRTAP, 2012; E-PRTR, 2012
0.027	0.172	LRTAP, 2012; E-PRTR, 2012
0	0.593	LRTAP, 2012; E-PRTR, 2012
0.070	0.476	LRTAP, 2012; E-PRTR, 2012
0.952	2.338	LRTAP, 2012; E-PRTR, 2012
0.272	7.540	LRTAP, 2012; E-PRTR, 2012
	2.222	LRTAP, 2012; E-PRTR, 2012
0.092	0.186	LRTAP, 2012; E-PRTR, 2012
0.022	0.011	LRTAP, 2012; E-PRTR, 2012
0.406	1.184	LRTAP, 2012; E-PRTR, 2012
		Suzuki, 2012, pers. comm.
		Seo, 2012, pers. comm.
0	0.012	LRTAP, 2012; E-PRTR, 2012
0		LRTAP, 2012
0.004		LRTAP, 2012
		Solórzano, 2012, pers. comm.
0.013	0.491	LRTAP, 2012; E-PRTR, 2012
0.127	0.063	LRTAP, 2012; E-PRTR, 2012
0.488	3.019	LRTAP, 2012; E-PRTR, 2012
0.017	0.323	LRTAP, 2012; E-PRTR, 2012
0.045	1.192	LRTAP, 2012; E-PRTR, 2012
0.323	0.241	LRTAP, 2012; E-PRTR, 2012
0.009	0.045	LRTAP, 2012; E-PRTR, 2012
0.365	2.095	LRTAP, 2012; E-PRTR, 2012
0.044	0.135	LRTAP, 2012; E-PRTR, 2012
0.115	0.387	LRTAP, 2012; E-PRTR, 2012
1.649	3.582	LRTAP, 2012; E-PRTR, 2012
		US EPA, 2012

this dialog resulted in feedback that refined the methodology, resulting in improved convergence of respective estimates and also improvements in the information base used to derive estimates for other countries. This is considered an ongoing process that can and should be continued.

Table 2.8 presents a comparison of nationally reported emissions with the estimates derived using the 2010 inventory methodology for relevant countries. This table presents only a comparison of the total national estimates for the countries concerned. Annex 7 includes more detailed comparisons, including (where possible) comparisons of estimates for individual sectors.

In the table, an attempt is made to distinguish national emissions estimates that can be directly related to sectors quantified in the 2010 global inventory, from other sectors that may or may not be included. Precise alignment of sectors used in different reporting systems is not straightforward (for example, see comments relating to LRTAP reporting in Table 2.1). The categorisations in the table below are therefore made employing a basic interpretation of sector descriptions; it was beyond the scope of the work to conduct a more detailed analysis of this aspect.

A number of pollution release inventories based on facility-level reporting rely on operators and industry to report emissions, and most also have an associated threshold for reporting (e.g., site Hg emissions > 5kg per year for the Canadian PRI, or >10 kg per year in the case of the EU's E-PRTR). An analysis of the point sources listed in the comprehensive US EPA national emission inventory for 2008 indicates that ca. 15% of the reported emissions are from plants emitting <10 kg/y and more than 8% from plants emitting <5 kg/y. Emissions reported under the E-PRTR (see Table 2.8) constitute approximately 35% of total emissions reported by the same countries under the LRTAP reporting system. In this case, it is not possible to gauge whether there are many facilities in Europe with emissions <10 kg/y or whether emissions are under-reported. This illustrates the importance of the need to be aware of the basis for reporting under different systems, the need for checking and auditing of reported emissions, and above all transparency in reporting if estimates are to be credible.

There are therefore a number of reasons why estimates of Hg emissions produced in the 2010 inventory may not fully agree with national inventories made by countries using other methodologies. These reasons include:

- Reporting schemes may define and distinguish emissions source sectors in very different ways, and aligning these sectors may not be possible.
- Industry reporting to national government may be limited to sources with emissions above a certain threshold level so that emissions from smaller sources, below the threshold, are not reported. Where smaller sources make up a significant part of the source category, reported inventories may therefore significantly underestimate total Hg emissions.

- National inventories in some countries are making increasing use of actual measurements of Hg emissions at individual facilities. Measurement-based estimates are typically lower than estimates based on mass-balance approaches. At the global scale it is not yet feasible to base an inventory on individual site emissions.
- National reporting and monitoring schemes may have access to information that is not available to externally produced inventories.

Notwithstanding these comments, given the significant uncertainties associated with all emissions estimates, and the fact that they have often been made using different approaches, the level of agreement between the 2010 global inventory and nationally reported estimates is, with a few exceptions, surprisingly good. For some countries, where national information was used directly in the calculations of the global inventory estimates, consistent results might be expected, however for others, including most European countries, the 2010 inventory estimates are dependent entirely on use of default factors and generalised assumptions in the global inventory methodology. This level of agreement is an encouraging verification for the methodology employed to prepare the 2010 inventory estimates.

2.3.3 Discussion of results for selected sectors

The following information supplements and updates information presented in the 2008 assessment technical background report (AMAP/UNEP, 2008).

2.3.3.1 Stationary combustion of fossil fuels

Coal combustion remains a major source of anthropogenic Hg emissions, comprising 24.2% of the estimated emissions in 2010, with oil combustion contributing a further 0.5%.

The differentiation of the contributions from combustion in power plants, industry and domestic/residential burning permits improved evaluation of the currently applied emission controls and thus potential benefits of future abatement strategies.

Similarly, use of activity data for different types of coal (and oil) allows for better introduction of appropriate emissions factors in the emission estimation procedures. The current differentiation includes four basic coal types: the hard coals (anthracite and bituminous), and the brown coals (lignite and sub-bituminous), see Figure 2.9.

From an emission calculation perspective, one issue that came to light in the current work that has perhaps been neglected in previous work is associated with the moisture content of some brown coals. Coal Hg content is widely used as a basis for emission factors when estimating emissions from coal burning. Mercury content is generally reported on a dry weight basis, however even in recent reports this is not always clearly stated and some measurements refer to coal 'as received' (i.e., wet weight basis). Hard coals contain little moisture, however, some brown coals – for example some of the coals burned in Australia – may have moisture contents as high as 50%. The implication is that emission factors based on dry weight Hg content may not be appropriate for coals burned while still containing high moisture content. For example, a coal with 100 ppm Hg content on a dry weight basis, and a moisture content of 35% has an equivalent Hg content of 65 ppm on a wet weight basis – if these coals are not dried before they are burned, and the 100 ppm Hg content is used in an emission factor, this could result in a more than 50% overestimation of the emissions.

2.3.3.2 Cement production

A new factor affecting the estimates of Hg emissions is the increasing levels of co-incineration of waste and use of alternative fuels in cement kilns. (Unabated) emission factors

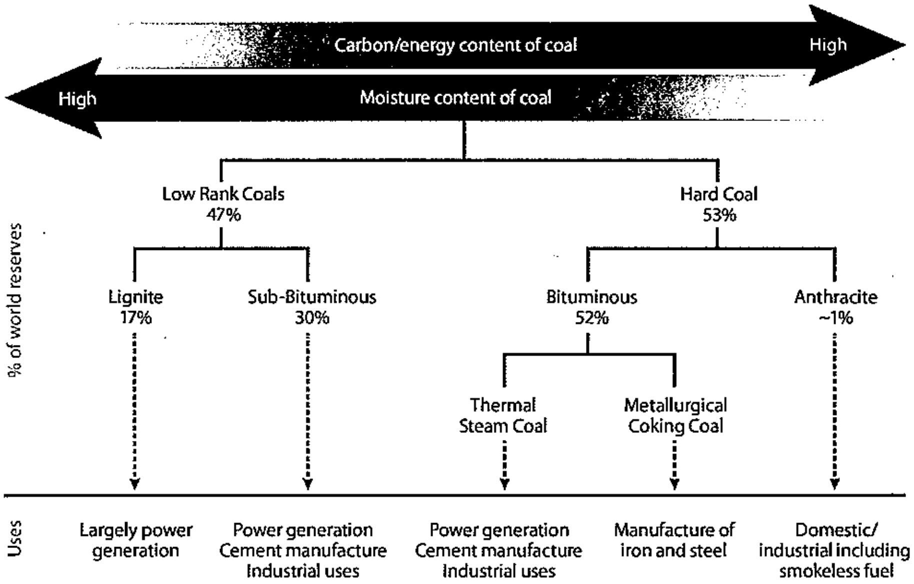

Figure 2.9. Coal types and their uses. Source: after World Coal Association.

associated with waste co-incineration are higher than those for use of coal, oil or petroleum coke alone as fuels in cement kilns (UNEP, 2011b), although regulations in some regions have been introduced to limit or prevent emission levels increasing as a result of this practice. In the United States National Emission Inventory (US EPA, 2012) some emissions from cement plants that are incinerating wastes are accounted under the hazardous waste incineration sector. To avoid double counting of coal and oil fuels, and to attempt to take account of fuel mixes and waste co-incineration in different countries, a number of nationally-relevant (unabated) emission factors were developed and applied in calculating emissions from cement production (see Annex 6). Bearing in mind that some of the emissions associated with fuels used in cement production are accounted elsewhere in the inventory, the emissions associated with cement production (ca. 8%) remain a major contribution in the global inventory. More information on use of alternative fuels and Hg emissions associated with waste co-incineration are required to reduce the uncertainties associated with emissions from cement production.

Recent trends in emissions associated with the cement sector are discussed in Section 2.4.7.

2.3.3.3 Iron and steel production

In the 2005 inventory, (abated) emissions factors were applied to steel production activity data. In the current inventory, estimates were produced based on production of (primary) pig iron including emissions from coke ovens, sinter plants, pellet plants, blast furnaces and basic oxygen steelmaking. Emissions associated with secondary steel production are only addressed in as far as the contribution from waste recycling that is accounted under the intentional-use sector emissions estimates.

The decision to focus on primary metal production was associated with the fact that electric arc furnaces do not have the Hg emission profile of blast furnaces, and an assumption was made that most scrap steel (raw material) would not be expected to contain much Hg. However, comparisons of the results obtained using this approach with estimates reported in national inventories indicates that, for most countries where such comparisons are possible, the national emissions estimates are higher. The national estimates generally do not distinguish between primary and secondary metal production and therefore also include emissions from secondary steel production.

Considering the United States and Canada, where national information provides some insight into respective emissions from primary and secondary steel production, it was surprising to note that the emissions from secondary production are apparently much higher than those from primary production. In the United States (2008) National Emission Inventory Hg emissions from primary and secondary steel production are 4530 and 577 kg, respectively; and in Canada 410 kg for primary + secondary compared with ca. 180 kg from primary production. If similar ratios were scaled to a global level this would imply a considerable under-estimation (by a factor of between 2 and 7.8) in the global inventory of emissions from the ferrous metal sector. One possibility is that Hg-contaminated scrap metals are entering the process. The UNEP Toolkit bases its emission factor for secondary ferrous metal production on numbers of recycled vehicles, which are assumed to contain ca. 0.2–2 g of Hg per vehicle from Hg-switches and lamps. However, these devices have mostly been phased out some time ago or (in some countries at least) should be removed prior to re-cycling vehicles. This issue warrants further attention and indicates that the estimate for emissions associated with primary ferrous (and possibly non-ferrous) metal production in the global inventory may be on the low side due to lack of quantification of secondary metal emissions.

Recent trends in emissions associated with the (primary) ferrous metal sector are discussed in Section 2.4.8.

2.3.3.4 Non-ferrous metal production

The estimates presented in the current inventory for emissions from copper (Cu), lead (Pb) and zinc (Zn) production take better account of differences between artisanal and large-scale production methods (especially those with integrated acid plants) than previous inventories. A number of assumptions have been made regarding in particular the Hg capture by acid plants (assumed at 90%) and air pollution control devices (APCDs) downstream of the acid plants, and estimates could be improved by better information concerning specific application of technology in different countries. A number of complicating factors, including co-production of non-ferrous metals add further uncertainty to estimates for emissions from non-ferrous metal production.

The 2010 inventory includes estimates of emissions from aluminium (Al) production that have not been assessed in previous inventories. These estimates assume Al production from bauxite, rather than alumina (an intermediate product, a subject of free trade between the countries), due to the lack of availability of Hg inputs and outputs for alumina-based Al production. However, available activity data on primary Al production does not specify whether the metal was produced from bauxite or from (imported) alumina. Aluminium-producing countries with bauxite production include Australia, Brazil, China, Greece, India, Iran, Kazakhstan, Russia, United States and Venezuela. For other countries with Al production a lower emission factor was applied, reflecting an assumption that these countries base (more of) their production on alumina rather than bauxite.

The unabated emission factor for Hg production adopted from the UNEP Toolkit is only applicable to countries with dedicated Hg production (from cinnabar). Emissions estimates for Hg production were therefore made only for those countries with production from Hg mining (China, Kyrgyzstan, Morocco, Russia and Tajikistan). In other countries where Hg is a by-product of gold production (Chile and Peru) or zinc production (Finland) there may be some associated emissions, but these are not separately quantified in the inventory. This may also be so for Mexico, where Hg is reclaimed from Spanish colonial silver mining waste.

Recent trends in emissions associated with the non-ferrous metal sector are discussed in section 2.4.8.

2.3.3.5 Large-scale gold production

Emission estimates from large-scale gold production (as distinct from production by ASGM) are considered preliminary and have large associated uncertainties. This reflects the fact that key information required for the calculation of emissions estimates – such as the gold content of ore, Hg content of ore, and amount of ore mined per tonne of gold produced – vary considerably both between and within countries – and over time. Representative information for individual countries is still largely lacking and therefore estimates are based on gross generic assumptions as described in Annex 6.

2.3.3.6 Chlor-alkali industry

Information on losses from the chlor-alkali industry in Europe is available from OSPAR (e.g., OSPAR, 2011) and from other countries through initiatives under UNEP and the World Chlorine Council (see UNEP, 2012). According to this information, there are around 100 chlor-alkali plants worldwide that still use Hg-cell technology, with associated Hg emissions to air. However, this number continues to decrease, as does the amount of Hg used per tonne of chlorine produced. Emissions of ca. 46 t of Hg from the chlor-alkali sector were reported in the 2005 inventory, compared with ca. 28 t in the 2010 inventory, and this trend is expected to continue as additional Hg-cell plants close or convert to other technologies. There are, however, still uncertainties relating to official information regarding emissions of Hg from the chlor-alkali industry and the fate of Hg unaccounted for in plant mass-balance calculations.

2.3.3.7 Oil refining

Emissions from oil refining have not been addressed in previous global inventories, and in the 2010 inventory are estimated to contribute a little under 1% of the total global inventory. This sector does not include emissions that may occur during extraction and transportation of crude oil and gas, or combustion of oil at refineries for power (which would be accounted under the industrial stationary combustion estimates). New information on Hg content of oils from different countries and regions was applied in developing revised emission factors that are being incorporated in revisions to the UNEP Toolkit.

2.3.3.8 Artisanal and small-scale gold mining

The estimate of Hg releases from artisanal and small scale gold mining (ASGM) is based primarily on field and industry reports from countries with active ASGM communities. The quality of the estimates ranges from good to reasonable to poor across the 72 countries known to have ASGM activities (see Annex 2, Table A2.1). A first-order estimate of the amount and location of Hg being released into the global environment (atmosphere, land and water) by ASGM is readily obtained with an average estimated uncertainty of ca. ± 43%. Because the estimate is maintained continuously and updated whenever possible (www.mercurywatch.org), the current estimate (for 2011/2012) can be assumed to be equal to or greater than the releases for 2010 since no reduction in ASGM activity and associated Hg use has been noted over most of the past decade.

It is estimated that ASGM releases in 2011 averaged 1610 t Hg/y (± 43.4%; range 910–2300 t/y) with 45.2% of this amount (727 t/y, range 410–1040 t/y) being emitted to the atmosphere. The remainder (880 t/y) was released to the hydrosphere (rivers, lakes, soils, tailings). However, a significant but unknown portion of the amount released into the hydrosphere is later emitted to the atmosphere when it volatilises (latent emissions). Results from historical gold rushes suggest that over a period of 100 years at least 70% of known inputs to the hydrosphere are subsequently released to the atmosphere. The 2010 estimate of emission to the atmosphere is significantly different to that reported for 2005 in the AMAP/UNEP (2008) assessment, both in terms of its magnitude and in the way the estimate has been made (see discussion in Section 2.4).

With a contribution of an estimated 727 t in 2010 to the global inventory of anthropogenic Hg emissions to air, ASGM sources are the largest contributing sector (37%); comparable to and slightly higher than fossil fuel combustion sources. ASGM emissions are dominated by sources in South America, Sub-Saharan Africa and East and Southeast Asia (see Figure 2.8).

2.3.3.9 Vinyl chloride monomer production

Although not included in the sectors quantified in the 2010 inventory, it is known that large quantities of Hg are used as a catalyst in the production of vinyl chloride monomer (VCM). A report developed by the China Council for International Cooperation on Environment and Development (CCICED, 2011) identified use of 800 t of Hg in this sector in China alone in 2012. Most VCM production is in China.

In 2009, a coal-based process was used at 94 of China's 104 VCM/PVC plants. From a use of between 540 and 970 t of Hg in the VCM/PVC industry in recent years, it was predicted that by 2012, China's VCM/PVC production would reach 10 million t with associated Hg consumption exceeding 1000 t. PVC production is planned to double between 2010 and 2020 (CCICED, 2011).

According to the CCICED (2011) report, little of the Hg used in VCM production is recycled; however, recent information from China indicates that the waste Hg catalyst is recyled and reused.

The ultimate fate of waste Hg catalysts from VCM production in China and elsewhere, and possible emissions to air and releases to water from Hg use in VCM are not yet adequately documented.

2.3.3.10 Dental amalgam

Emissions from use of Hg in dental amalgams resulting from cremation of human remains are estimated at 3.6 t (range 0.9–11.9 t) in 2010 globally (see Section 2.3.1). This estimate does not include Hg emissions associated with releases during production and preparation of Hg amalgam fillings and disposal of removed fillings. It is estimated that ca. 20–30% of total Hg consumption for dental uses (that is 70–100 t of the estimated 340 t of Hg currently used in dental uses) is likely to enter the solid waste stream. In addition, Hg in removed fillings goes to recycling, solid waste and wastewater (P. Maxson, pers. comm.).

A recent European Commission report (EC, 2012) estimated EU Hg demand for dentistry (in 2010) at around 75 t/y (range 55–95 t/y), of which about 45 t/y ends up in dental surgery effluents; only part of this is captured and treated as hazardous waste in compliance with EU legislation. According to this report, dental Hg waste constitutes some 21–32% of overall EU Hg emissions to air and up to 9–13% of overall EU emissions to surface waters. The estimates of EU Hg emissions to air from crematoria used in this report (based on national reporting) are somewhat higher than the estimates in the 2010 inventory (maximum estimate ca. 1.1 t/y). This may indicate that, for example, the effectiveness of Hg emissions reductions due to control devices at crematoria in Europe has been overestimated in the 2010 inventory. However, this component of emissions to air has acknowledged high uncertainties, and emission factors and methods applied in different countries to estimate crematoria emissions vary considerably.

2.3.3.11 Fate of mercury removed by abatement technologies

Bearing in mind that many assumptions have been made regarding application of APCDs for the different sectors and countries, the results of the 2010 inventory imply that (from the difference between total unabated and abated emissions estimates) almost 3000 t of Hg are removed by currently installed APCDs (including removal by integrated acid plants at non-ferrous metal smelters). This amount does not include Hg removal by processes such as coal washing, or Hg removal by other systems designed to reduce Hg contamination that are not directly linked to air emissions.Control technologies installed at industrial facilities remove Hg that would otherwise be emitted to air. There is little information about the ultimate fate of the Hg removed in this way and about how the Hg-containing wastes are subsequently disposed of. Some of the Hg is recovered and re-enters the market supply, or is stockpiled. Some of the Hg removed by APCDs will be associated with materials such as fly-ash that may be disposed of in landfill or used in production of building materials (plaster board, road surfacing materials, cinder/breeze blocks, etc.). Mercury 'recycled' into construction materials is generally considered 'inert', however some Hg will almost certainly be re-emitted or leach into aquatic systems if, for example, landfills are not properly constructed. In general, it can be assumed that these technologies will reduce the amount of Hg that is transported long distances, by concentrating it, at least temporarily, in materials that are disposed of or used within the source regions themselves.

2.3.4 Geospatial distribution of the 2010 inventory

Products of the 2010 global inventory project work include a geospatially distributed (gridded) version of the inventory of anthropogenic Hg emissions to air, for use in modelling and other related applications. The approach used to produce the gridded inventory followed a general methodology used previously and described by Wilson et al. (2006) and AMAP/UNEP (2008), whereby emissions are assigned to point sources where possible, with the remainder being (spatially-) distributed according to the distribution of some appropriate surrogate parameter such as population density; with the combined results then allocated to cells in a 0.5 × 0.5 degree grid.

Previous work has developed a model for performing this task based on the construction of several 'distribution masks' for application to emissions from different sectors. These 'distribution masks' were updated in the current work. A recognised deficiency of previous work was the limited extent of the information concerning point source emissions. Allocation of emissions to specific point sources is the most precise way of geo-spatially distributing emissions, in particular those associated with industrial and energy sources; however, point source information in the past has been largely restricted to a few countries for which plant specific pollution release inventories or emissions inventories are available, namely the United States, Canada, Australia, and EU Member States. A major effort under the current work, therefore, has been to extend the point source coverage to other major emitting countries, using new resources and information made available through the project contact group.

Point source data for the different sectors were compiled from a variety of available sources, some comprising national/regional release inventories (as mentioned above) and others based on industry group (web-based) resources or other public domain information resources. These were supplemented with national information where available. The work to prepare a comprehensive, register of point sources useable for distributing Hg emissions involves a number of steps, not least of which is filtering or cleaning the information from multiple sources to remove duplicates, and where possible to correct for obvious errors. Many of the available resources are poorly quality-controlled and inconsistent use of, for example, Mt as an abbreviation for mega-tonnes and metric tonnes in relation to plant capacity or fuel use is one of the commonly occurring issues that needed to be addressed (and which can be, based on reasonable assumptions).

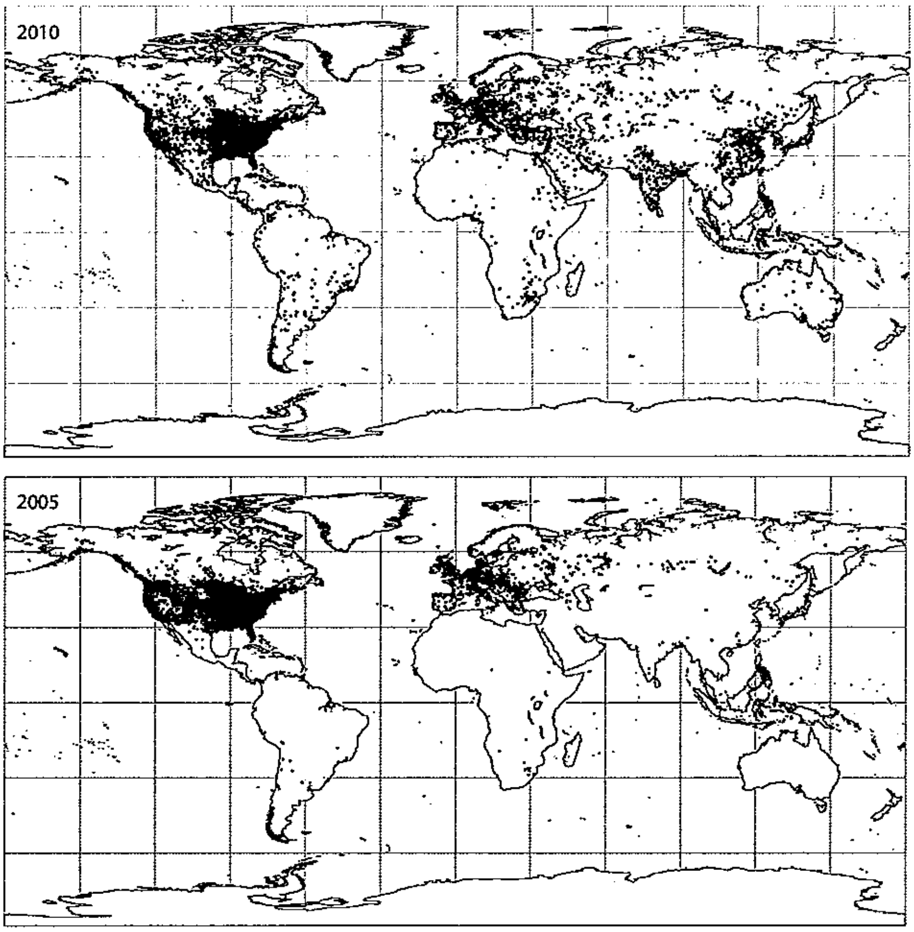

Figure 2.10. Maps showing the increase in the number of mercury point sources utilised in the geospatial distribution of the 2010 global inventory (above) compared with those utilised in the 2005 global inventory (below) spatial distribution work.

Key information required for each point source includes its location, the sector in which it operates (ideally including information on fuel use, etc.), and its associated Hg emission, or some information that can be used to allocate a portion of the total national emission for a given sector to that particular source. In order to apportion (national total) emissions between point sources relevant for the sector concerned the following procedure is followed: (1) In cases where a plant is listed in a national emissions inventory and/or in an official government report which include an applicable (2008–2010) Hg emission, the reported emission value is assigned to that plant. In many cases, however, while basic information concerning a point source is available – Hg emissions data are lacking. Commonly the situation is that some plants within a country have associated emissions, while others do not. In these cases the total national emissions for a given sector – or that part remaining after subtraction of the amount assigned to plants with reported emissions – is distributed between the plants without reported emissions. This is done by (2) weighting the emissions assigned to a given plant by some appropriate factor. Generally this factor is plant capacity – information on which is often available. For plants with no known capacity, an average capacity is calculated from the information for other plants in that country. When neither emission nor capacity is known for any of the plants in a country, the emissions for the sector concerned are distributed evenly between the plants in that country. Any national emissions remaining after distribution (which can be the case if some point sources lack critical information such as location coordinates) is added to the county's 'diffuse emissions' for the sector and handled by the geospatial distribution model accordingly.

This procedure recognises a number of assumptions, such as the fact that reported plant capacity may not necessarily provide a good indication of a plant's actual operations, however, this information is used in relative rather than absolute terms and the gains using these assumptions are considered preferable to other assumptions that would otherwise be involved in the spatial distribution process.

Figures 2.10 and 2.11 present some of the results of this component of the work.

It is worth noting in this connection that this procedure reveals apparent discrepancies between emissions assigned to point sources in some national/regional pollution release inventories and those allocated on the basis of the national emissions estimates produced in the current work. The implications are either, in some cases, considerable over-estimation of emissions from some sectors in the current work – which is not consistent with the generally good agreement between the estimates produced and those reported in official national inventories – or a considerable under-estimation of point source emissions reported in some pollution release inventories. These discrepancies warrant additional work, but it was beyond the scope of the current project to address this in any detail.

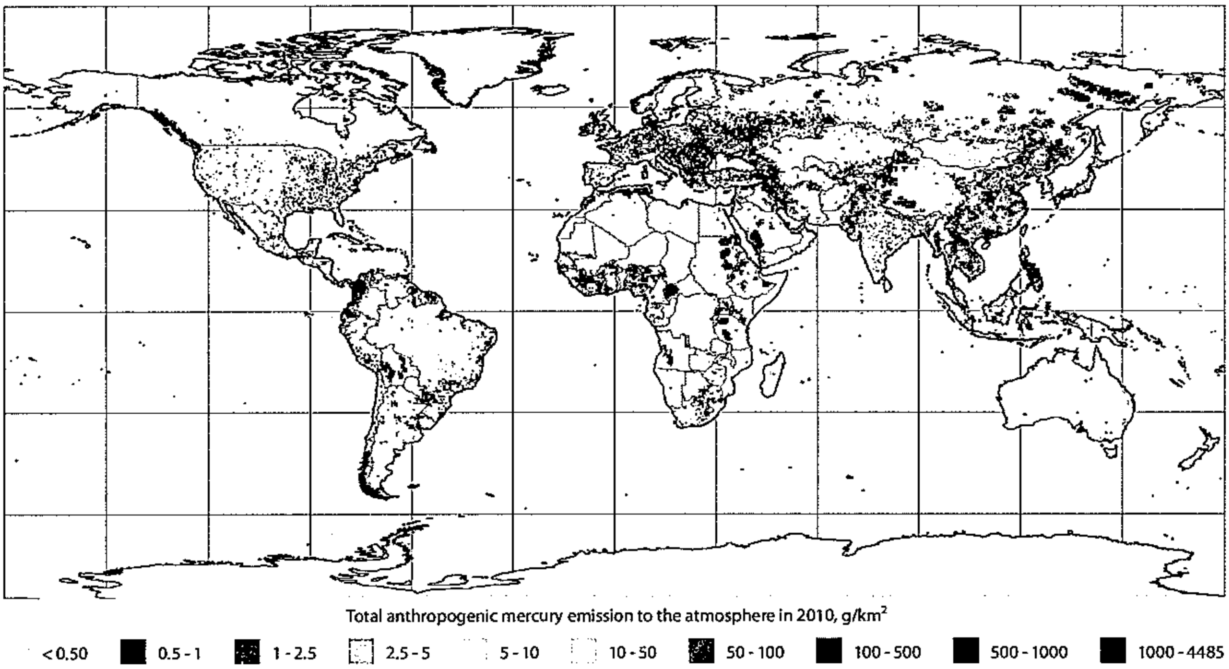

Figure 2.11. The geospatially distributed 2010 global inventory of anthropogenic mercury emissions to air (does not include emissions from contaminated sites).

2.4 Trends in mercury emissions to the atmosphere

2.4.1 Comparing emission inventories over time: Reasons for caution

Owing to the factors described in Section 2.2.2, it is not appropriate to directly compare results from different global inventories prepared at different times using different methods and assumptions. However, this has not prevented such comparisons being made.

Therefore it is relevant at this point to reiterate a KEY MESSAGE: that the emission estimates derived from this work CANNOT be directly compared with those from previous global emission inventories. Such comparisons may be inappropriate and could lead to erroneous conclusions regarding emission trends.

In order to compare global anthropogenic emissions inventories produced between 1990 and 2010 it is necessary to take into account two main issues: changes in the methodology used (including sources of activity data), and the introduction of additional sectors in more recent inventories.

In the past, some tentative comparisons of global anthropogenic emission inventories produced between 1990 and 2005 have been made based on the (somewhat) internally consistent approaches used to produce these inventories. Some tentative comparisons can also be made between 2005 and 2010 results for certain sectors. The following discussion of these comparisons illustrates some of the complicating factors that need to be taken into account when comparing inventories produced at different times.

2.4.2 Trends in emissions 1990–2005

Because the 2005 global inventory introduced major new emissions sectors compared with earlier inventories, an attempt was made to produce a harmonised set of global inventory estimates (1990–2005) by applying the 2005 methodology to the activity data from earlier years, and comparing emissions for a comparable set of emission sectors based on more consistent activity information (AMAP, 2010; UNEP, 2010a). Although this approach is compromised by the fact that it does not address the (possibly) significant changes in (abated) emission factors that would be expected over the period 1990–2005 in some countries (especially in Europe and North America) due to changes in technology, it did address some of the artefacts of different approaches and data components used in constructing past global emission inventories. The results of this work, illustrated in Figure 2.12 and included in

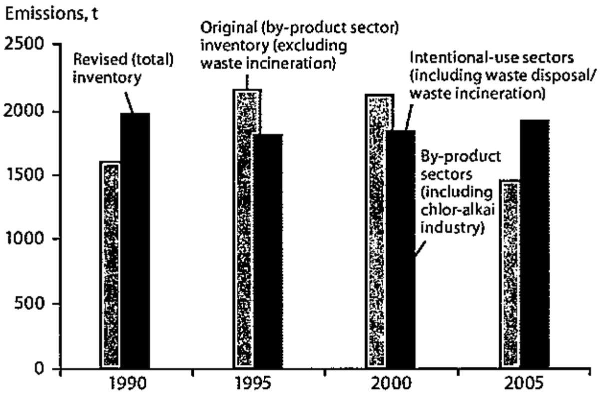

Figure 2.12. Revised estimates of total global anthropogenic mercury emissions to air from by-product and intentional-use sectors for the period 1990–2005, showing the effect of re-calculation using the 2005 methodology. Source: AMAP (2010).

Table 2.9. Comparisons of past and present global anthropogenic mercury emission estimates (in tonnes) produced using different procedures (see also Table 2.10).

	1990	1995	2000	2005	2010
Originally published inventory estimates	1732[a]	2214[a]	2190[a]	1926[b]	
Inventory estimates revised using 2005 methodology	1967[b]	1814[b]	1819[b]	1921[b]	
of which ASGM				350	
Inventory estimates produced using 2010 methodology					1960
of which ASGM					727
Coal combustion				462[c]	474
Cement				133[c]	173
Pig iron and steel				36.7[c]	45.5
Non-ferrous metals (Cu, Pb, Zn, Hg)				169[c]	200
Large-scale gold production				98.3[c]	97.3
Waste from Hg-containing products				112[c]	95.5
Other sectors					145[d]

[a] By-product sectors only (plus waste incineration in Europe (EU countries), Canada and the USA; [b] by-product and intentional use sectors (including ASGM) combined (Table modified from AMAP, 2011); [c] estimate produced using 2010 methodology on 2005 activity data from essentially the same sources as those used in 2010; [d] includes sectors not quantified in previous inventories.

Table 2.9 (1990–2005), reveal possible underlying trends in global anthropogenic emissions that are very different from those that would appear to exist if total emissions reported for past global inventories are compared at face value.

2.4.3 Trends in emissions 2005–2010

In a similar manner, it is possible to use the databases developed to prepare the 2010 inventory to 'simulate' the emissions that would have been derived using 2005 activity data (for some emission sectors at least). Results for emissions from coal combustion, cement, ferrous, and non-ferrous metal sectors and from wastes from Hg-containing consumer products using this approach are also included in Table 2.9. It is important to note that this 'simulation' is based largely on activity data alone and does not take proper account of possible changes in abatement technology from 2005 to 2010. Results for some individual sectors are discussed in more detail in following sections.

When these revised estimates are combined with 2005 estimates for some additional sectors (ASGM, crematoria, and chlor-alkali industry) it is possible to compare 2005 and 2010 results on a more consistent basis. It should be noted that this analysis does not include sectors that were introduced for the first time in 2010; however, the major emission sectors (accounting for some 95% of the total 2010 global inventory) are included. The results shown in Figure 2.13 illustrate the implied changes in emissions between 2005 and 2010 from different sub-regions for three different groups of sectors (representing industrial by-product emission sectors, ASGM and intentional-use and waste sectors, respectively).

One obvious feature in these comparisons is the significant change in the estimates associated with ASGM. In this case however, the difference is not (directly) associated with changes in activity, but rather with changes in reporting and emission evaluation methods, as discussed in Section 2.4.4. This highlights the caution that needs to be applied and the pitfalls associated with superficial comparisons of estimates derived at different times using different methods and data sources.

Notwithstanding the implications of changes in methodology for evaluation of emission trends, the new methodology applied in 2010 is considered to result in more reliable estimates of global anthropogenic Hg emissions, and the new methodology also introduces procedures that should make it possible to better identify and correctly attribute trends in future emissions estimates – avoiding some of the factors that confuse the picture when comparing previous inventories.

2.4.4 Interpreting apparent 2005–2010 trends in emissions – using the example of artisanal and small-scale gold mining

As discussed in the previous section, results presented in the AMAP/UNEP (2008) report and the current report (see Section 2.3.1) imply considerably increased Hg emissions from ASGM from 2005 to 2010; raising the question of what is responsible for this increase?

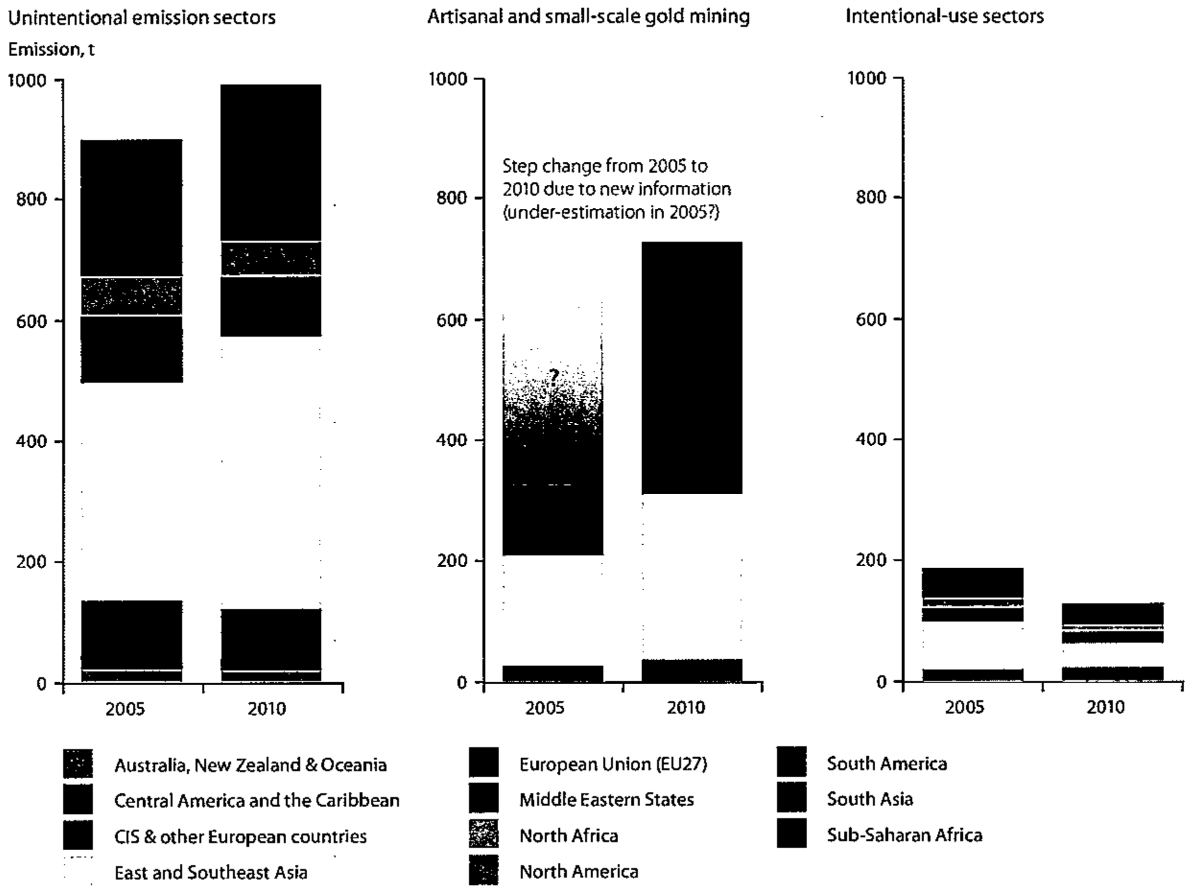

Figure 2.13. Comparison of 2005 and 2005 estimates of emissions to air from different regions, based on application of the 2010 inventory methodology. Unintentional emission sectors: Coal burning, ferrous- and non-ferrous (Au, Cu, Hg, Pb, Zn) metal production, cement production. Intentional-use sectors: Disposal and incineration of product waste, cremation emissions, chlor-alkali industry.

Although it is likely that there was more ASGM taking place in the world in 2011 than in 2008 due to the increased price of gold and increased rural poverty, the increase in the Hg emission estimate presented in the Burkina Faso case study (see Annex 2) is predominantly due to improved reporting. Similarly, the implied increase in global ASGM Hg emissions is also mainly due to more and better data for countries for which the emissions were previously poorly estimated, such as the West African countries which were formerly only reported as having a presence of ASGM and therefore assigned a minimal value of 0.3 t/y. In other words, the baseline has been improved.

2.4.5 Interpreting apparent trends in emissions – other main sectors

One of the most important consideratons when evaluating trends in (anthropogenic) emissions is to consider whether these make sense in relation to changes that may be expected based on, for example changes in economic activity, technology, fuels and raw materials or regulations. From the previous discussion, it can be concluded that any 'real' changes from 2005 to 2010 in Hg emissions associated with ASGM activities are likely to be masked by the effects of changes in reporting and estimation procedures. Such issues need to be given careful consideration in any evaluation of emission trends.

The AMAP (2011) assessment concluded that global Hg emissions to air have been fairly constant since around 1990, but with emissions decreasing in Europe and North America and increasing in Asia. In 2005, East and South East Asia contributed about 50% of global Hg emissions to air from human sources, and there were indications that, after decreasing from a peak in the 1970s, global emissions from human sources may be starting to increase again.

For some of the main anthropogenic emission sectors, emission estimates for 2005 have been re-calculated using the 2010 methodology; applying it to activity data for 2005. It should be noted that these results do not take into account changes in application of emission abatement technology over the period – essentially assuming the abatement technology applied in 2005 was the same as that applied in 2010. It is likely that in some regions (including parts of Asia), some improvements in appplication of abatement technology were implemented between 2005 and 2010. This would result in some under estimation of the re-calculated 2005 emissions, but (based on sensitivity of estimates to changes in technology profiles) it is not considered likely that this would greatly alter the implied trends.

Table 2.10. Regional emissions (in tonnes) from selected sectors, and changes from 2005-2010 (based on application of 2010 inventory methodology).

	Coal combustion			Cement production			Ferrous metal production		
	2005	2010	% Change	2005	2010	% Change	2005	2010	% Change
Australia, New Zealand & Oceania	3.9	3.6	-8.2	0.7	0.7	0.0	0.04	0.04	0.3
Central America and the Caribbean	10.3	3.5	-65.5	3.3	3.2	-4.1	0.3	0.3	13.2
CIS & other European countries	35.0	26.9	-23.1	4.7	4.7	-1.1	7.8	7.5	-4.6
East and Southeast Asia	182.3	206.3	13.2	72.9	102.4	40.5	18.7	28.2	51.3
EU25	57.5	44.1	-23.4	14.4	13.1	-8.7	3.0	2.5	-17.0
Middle Eastern States	8.0	10.5	30.8	9.3	13.4	43.7	0.4	0.4	23.5
North Africa	1.0	0.5	-53.2	5.8	7.9	35.7	0.1	0.1	-36.1
North America	50.5	43.4	-13.9	3.4	2.3	-33.6	1.5	1.1	-25.0
South America	3.3	2.2	-33.0	3.8	5.1	35.3	3.2	3.0	-3.9
South Asia	70.8	90.8	28.2	11.6	16.9	45.4	1.4	2.0	40.2
Sub-Saharan Africa	39.6	42.6	7.6	2.8	3.4	24.0	0.3	0.3	-15.7
Total	462.2	474.3	2.6	132.7	173.0	30.4	36.7	45.5	24.0

Results and comparisons are tabulated in Table 2.10. These results indicate that emissions from some of the main 'industrial 'sectors have increased by up to 30% from 2005 to 2010, but with significant differences between regions, with decreases in some regions and increases in others (Asia in particular). For the waste sectors, trends indicate decreasing emissions in all regions. The possible reasons for some of these developments are discussed below.

2.4.6 Coal combustion

From an overall activity perspective, coal burning continues to increase, especially in China (see Figure 2.14); at the same time, however, improvements are being made in efficiency of energy production, and the application of air pollution control technology at power plants (including new power plants being constructed in China and in other parts of the world). These improvements are offsetting to a large extent the increase in Hg emissions that would otherwise result from the increase in coal combustion.

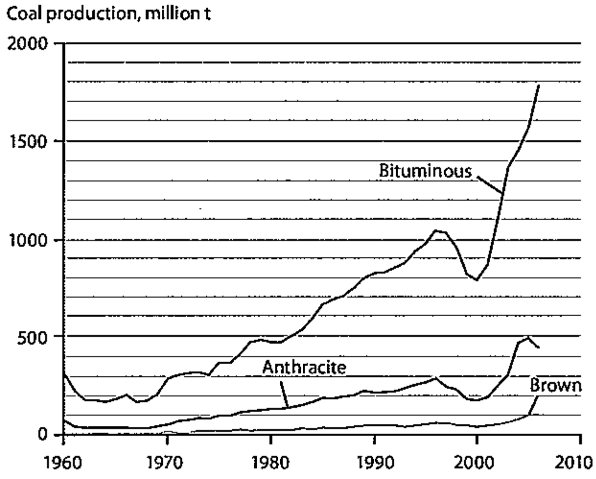

Figure 2.14. Trends in coal production in China. Source: Based on International Energy Agency data.

In the United States, emissions associated with stationary combustion (mainly coal burning) at electricity generating units have reportedly decreased from ca. 53 t in 2005 to 26.8 t in 2008 (US EPA, 2012). This is partly explained by the installation of Hg controls to comply with state specific rules and voluntary reductions, and the co-benefits of Hg reductions from control devices installed for the reduction of sulphur dioxide and particulate matter as a result of state and federal actions, such as New Source Review enforcement actions (US EPA, 2011a,b). A major factor may also be a change in the source of the coals used, with power plants using more low sulphur coals (with lower Hg content) in order to comply with new air pollution regulations. These documents project that US emissions from this sector will be further reduced by 2016.

2.4.7 Cement production

On the basis of activity data taken from the USGS Minerals Yearbook (USGS, 2012), cement production between 2005 and 2009 increased by almost 30% (Figure 2.15); however with large differences between sub-regions. Production in Europe, Oceania and North and Central America remained stable or declined, whereas in South America, the Middle East, Africa, and in particular Asia production increased. The consistent trends in emissions indicated in Table 2.10 are therefore mainly a reflection of these changes in activity.

Non-ferrous metals (Cu, Pb, Zn, Au, Hg)			Waste (from consumer products)		
2005	2010	% Change	2005	2010	% Change
18.5	16.7	-9.9	0.7	0.7	-0.9
8.3	11.7	40.9	4.0	3.4	-14.3
42.9	42.2	-1.7	8.3	7.1	-13.8
86.5	114.5	32.4	44.7	36.8	-17.8
14.4	11.7	-18.3	6.8	6.0	-12.4
3.8	3.9	0.8	5.2	4.5	-13.0
0.8	0.9	1.0	2.6	2.4	-9.1
3.5	3.2	-6.5	7.6	6.2	-17.7
39.8	38.7	-2.7	8.7	7.6	-13.0
11.3	22.3	96.9	19.0	16.7	-12.1
37.2	31.8	-14.5	4.7	4.2	-9.7
267.1	297.7	11.5	112.1	95.5	-14.8

2.4.8 Ferrous and non-ferrous metals

Emissions from ferrous metal production (also largely reflecting activity data), decreased in Africa, Europe and North Amerca, and to a lesser extent South America, but increased by more than 40% in both South Asia and East and Southeast Asia (Table 2.10).

The trends described in Table 2.10 indicate increases in emissions associated with non-ferrous metal production in East and Southeast Asia and in particular South Asia. In absolute terms the increase in (activity and associated) emissons in East and Southeast Asia is by far the greatest, however in relative terms the increase in South Asia is notable and due largely to production increases in India. In Central America and the Caribbean, the large percentage increase is associated with emissions from large-scale gold production.

2.4.9 Comparing emission trends and observations

Over longer time scales, Hg levels in environmental archive samples such as ice cores have been correlated with emissions of Hg to the environment (see Figure 2.16).

Recent trends in emissions to the atmosphere can also be compared with trends in Hg levels observed at atmospheric background monitoring sites (see Figure 2.17). This graphic illustrates that reliable air monitoring time series began only relatively recently, with little change in global emissions over the period concerned.

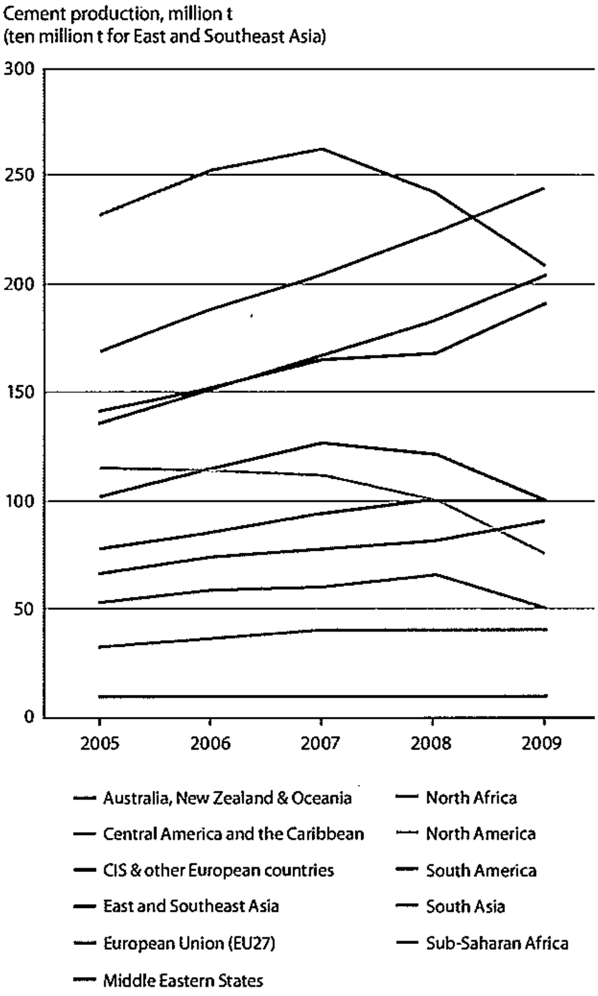

Figure 2.15. Trends in cement production. Note: different units for East and Southeast Asia. Source: United States Geological Survey.

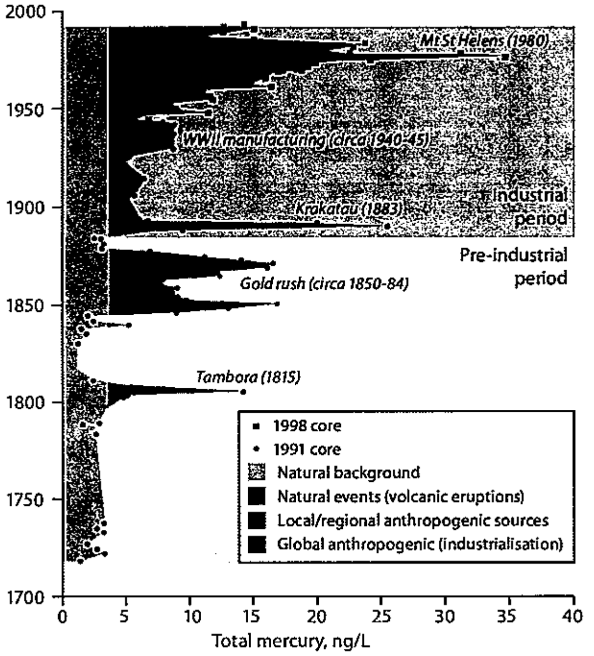

Figure 2.16. Ice core record of deposition from Wyoming, USA. Source: after Schuster et al. (2002).

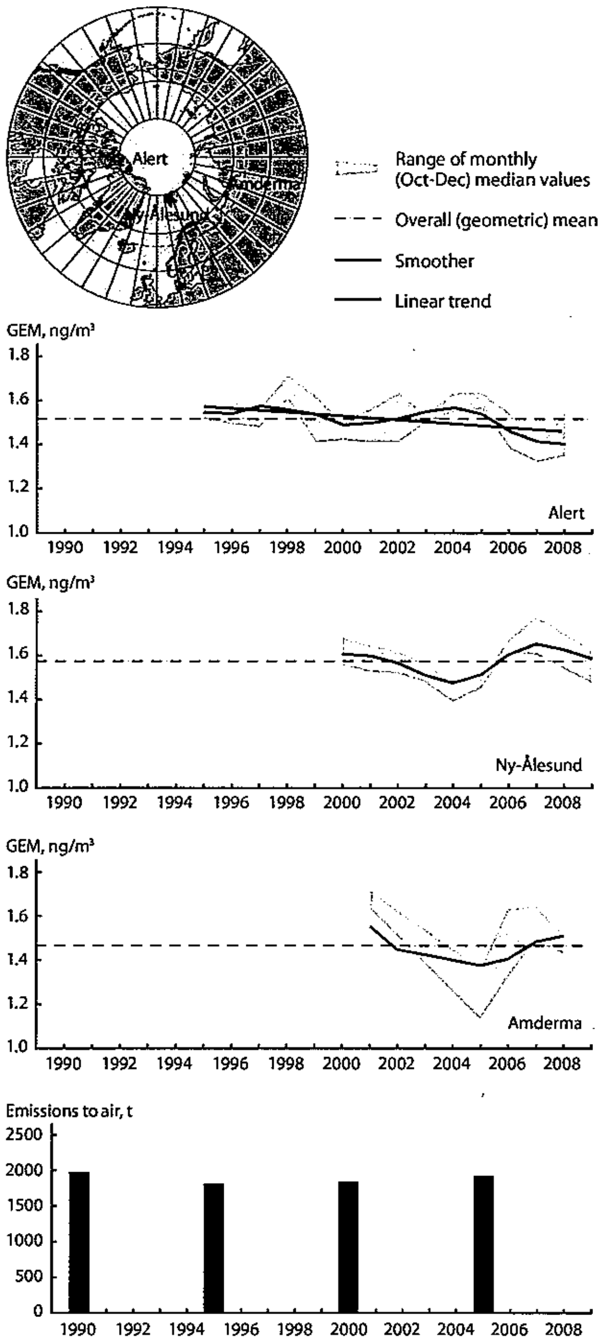

Figure 2.17. Trends in emissions (see Figure 2.12) and observed gaseous elemental mercury concentrations at Arctic background air monitoring sites. Source: after AMAP (2011).

2.4.10 Scenarios and identifying areas for targeting reductions

The 2008 *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* report (UNEP Chemical Branch, 2008; AMAP/UNEP, 2008) included a first attempt at producing global emissions inventories for future scenarios representing status quo (business as usual), extended emissions control, and maximum feasible technological reduction. At the time this was presented as very provisional work.

Since 2008, additional studies have presented estimates of global Hg emissions based on future scenario projections, for example, Streets et al. (2009) uses four IPCC (Intergovernmental Panel on Climate Change) scenarios of energy growth and technology to project global Hg emissions in 2050 in the range 2390–4860 t, representing a change of -4% to +96% compared to their estimate of 2480 t in 2006.

In addition to suffering from the same limitations as previously discussed concerning universal application of a single (abated) emission factor for a given sector, the scenario inventories presented in the 2008 report were criticised for the fact that they also made generic assumptions regarding the extent to which additional Hg reductions could be achieved within countries in various (continental) regions. That is to say, it was assumed that the same level of (further) Hg emission reductions could be achieved in advanced as well as less advanced countries within a region – despite some advanced countries probably having already largely implemented some of the 'future' emission control technologies. In part this reflected the fact that emission inventory systems in the past included very little information on actual implementation of technology in individual countries. Addressing this deficiency was one of the goals of the procedures and database systems established to produce the 2010 inventory.

Using the new database methodologies it should now be possible to implement scenarios involving both activity and technology components – that is, effects of economic development and fuel mix projections, etc. on activity levels, combined with effects of realistic projections on implementation of additional Hg emission controls to those currently in use – at an individual country level.

It has not yet been possible to complete new work on scenario emission inventory estimates based on use of the databases established to support the production of the 2010 emissions inventory – however this work is currently planned as part of the GMOS (Global Mercury Observation System) project work (see Section 3.3.5 for more details).

This includes possible use of the databases that have been constructed by countries to investigate the changes in calculated national emissions that would result from implementing different strategies, for example, by adjustment of their applied technological profiles, or changes in raw materials.

The economic crisis of 2008 led to stagnation and decreased economic activity in much of the world post-2008; with notable exceptions in some Asian countries and countries in parts of South America. However, even in the countries with continuing growth, this was lower than anticipated at the time the scenarios presented in the AMAP/UNEP (2008) report were prepared. The stagnation of economic development in a number of regions of the world is reflected in activity data for several Hg emission sectors related to energy and industry and this is in turn reflected to some extent in emission trends from 2005 to 2010.

2.5 Conclusions

2.5.1 Key findings on global emissions of mercury to the atmosphere

A new improved methodology has been developed to prepare an inventory of Hg emissions to air from anthropogenic sources in 2010 that allows better characterisation of differences between countries in terms of fuels and raw materials used and technologies and practices applied. Applying this methodology in a consistent manner globally results in an estimate of anthropogenic emissions to air in 2010 of 1960 metric tonnes (range 1000–4070 t).

Emissions estimates, whatever their basis, have large associated uncertainties; this remains the case despite the considerable progress that has been made in recent years in improving the knowledge base available for the development of emissions factors, etc. Quantifying uncertainties is difficult in light of the numerous assumptions involved in any estimation process. Crude estimates of uncertainties indicate that these can be from ca. ± 30% to more than an order of magnitude, depending on the sector/country concerned. Low- and high-range values associated with the 2010 global inventory reflect these uncertainties and are intentionally wide to reflect the still poor state of knowledge about some key factors involved in estimating Hg emissions.

The main sectors identified as sources of anthropogenic emissions to air in 2010 are artisanal and small-scale gold mining (ASGM), coal combustion, production of ferrous (iron and steel) and non-ferrous metals (including copper, lead, zinc, aluminium and large-scale gold production), and cement production. Other important sectors include incineration and disposal of wastes from consumer products containing Hg, emissions from contaminated sites, chlor-alkali industry emissions, oil refinery emissions, emissions from combustion of oil and natural gas, and from human cremation (associated with use of Hg in dentistry).

The 2010 emissions inventory covers most of the major anthropogenic sources of emissions to air, and includes some sectors not previously quantified. However, there remain potentially important sources that are still not yet quantified in the inventory. These include: use of Hg in vinyl-chloride monomer production; emissions from secondary metals production and ferro-alloys; oil and gas extraction, transport and processing other than refinery emissions; production and combustion of biofuels; emissions from industrial and some hazardous waste incineration and disposal; emissions from sewage sludge incineration; emissions during preparation of dental amalgam fillings and disposal of removed fillings containing Hg.

The sectors responsible for most emissions to air are the same as those previously identified; however, the estimated emissions associated with ASGM are significantly higher than previously estimated. This is attributed mainly to new information on use of Hg in ASGM in certain regions, in particular Sub-Saharan Africa. The implication is that emissions from ASGM may have been under-estimated in 2005. Due to the largely unregulated and in some cases illegal nature of ASGM, the associated emissions estimates are very uncertain and should be treated accordingly. Observational and measurement data to confirm high releases in areas of ASGM are lacking and represent a gap that should be filled.

The increase in emission estimates for ASGM has altered the proportional contribution of different sectors to the total global anthropogenic emissions compared with those presented in the AMAP/UNEP (2008) assessment; however, although fossil fuel (mainly coal) combustion emissions have decreased from ca. 45% (2005) to ca. 25% (2010), in absolute terms the emissions associated with coal combustion from major use in power plants and industry have remained fairly stable and may have increased slightly between 2005 and 2010. Emissions estimates for other coal uses, including domestic and residential coal burning, indicate these may have been over-estimated in previous inventories, due largely to assumptions regarding the relative amounts of coal burned in the power vs. domestic/residential sectors in some countries.

The major source region for anthropogenic emissions to air continues to be East and Southeast Asia (ca. 40% of the global total) with South Asia contributing a further 8%. The percentage contributions from South America and Sub-Saharan Africa are increased due to the increased estimates of emissions from ASGM.

Any evaluation of trends in emissions needs to take account of artefacts that can arise from changes in reporting and methods used to produce inventory estimates. Changes in methods and data and information sources and the introduction of additional sectors invalidate direct comparison of the results of global emission inventories produced over the past 25 years. Preliminary attempts to re-calculate emissions in 2005 using components of the new methodology allow some comparisons to be made of changes in emissions from 2005 to 2010. The results indicate that summed emissions from largely industrial sectors (fossil fuel combustion, metal and cement production) are continuing to increase while emissions from some other sectors (such as the chlor-alkali industry) continue to decline.

Examination of environmental archives indicates that anthropogenic Hg emissions are likely to have peaked around the late 1970s. Comparisons of emission trends since 1990, based on rescaling emission inventories for the period 1990–2005, gives some indication that anthropogenic Hg emissions to air, although generally stable at around 2000 t/y may be increasing slightly again, with decreases in emissions in some regions (e.g., Europe and North America) being offset by increases in others (in particular Asia). Results of the 2010 inventory do not contradict this possibility. The implied changes in emissions reflect in general terms the patterns of regional economic development during the period from 2005 to 2010, with continued economic growth in, in particular Asia and stagnation (following the 2008 economic crisis) in much of Europe and North America. The global economic crisis during the latter part of the past decade has resulted in emissions in some regions decreasing more, or increasing less than anticipated in scenarios presented in the 2008 assessment (AMAP/UNEP, 2008).

Trends in atmospheric Hg levels measured at some background sites where relatively long-time series exist (e.g., Alert in northern Canada, Amderma in northern Russia, and Mace Head in western Ireland) show generally decreasing levels of atmospheric Hg, although this is not observed at some other sites (e.g., Ny-Ålesund on Svalbard). Monitoring site location in relation to major emission source regions and time lags in possible environmental response to changes in emissions may be important factors that need to be taken into account when interpreting trend results at monitoring sites.

Estimates obtained using the global methodology generally show good agreement with national estimates, in some cases produced using very different approaches, on a national total basis. Agreement for individual sectors was more variable, in particular in the case of comparisons with the LRTAP based estimates, however many of these discrepancies can be attributed to differences in the way emission sectors are categorised, specified and employed in reporting under different systems. Comparisons were made with national inventories provided by several countries (Australia, Canada, Japan, Korea, Mexico and the United States, and European countries reporting to the LRTAP Convention). The results of these comparisons lend a degree of confidence to the generic assumptions applied, at least for some of the country-groups. The level of agreement is best for those countries that routinely produce their own detailed emission inventories, and where the information base is correspondingly most comprehensive. It was not possible to make direct comparisons with emission inventories developed using the UNEP Toolkit because many of these inventories refer to different years with different corresponding activity data, and/or were developed using default emission factors that are being revised based on information acquired during the preparation of the 2010 global inventory.

If reporting systems are to be compared, they need to be more specific and better aligned in terms of the sources that need to be distinguished.

National emissions estimates from some countries based on individual facility reporting and site measurements should be more accurate than those based on the global inventory methodology. However, this is difficult to evaluate as most nationally reported inventories lack estimation of associated uncertainties. It is also important to recognise that many measurement-based estimates are derived from relatively few measurements covering short periods that are then extrapolated to produce annual emissions. It is therefore important that such reporting is subject to validation and that associated uncertainties are quantified. In general, an evaluation and quantification of uncertainties should be a routine component of emissions reporting systems.

The contributions from experts from a number of countries, and discussion of discrepancies between the global estimates and estimates from national and industry sources proved an essential part of the work to prepare the global emissions inventory, and significantly improved the methodology. The results of these discussions are in turn being used to inform the work to revise and update the UNEP Toolkit for identification and quantification of Hg releases.

The 2010 estimate of emissions to air from anthropogenic sources is consistent with the values used in global models that attempt to represent global Hg cycling and global Hg budgets. According to these models, current anthropogenic sources contribute ca. 30% of total annual emissions to air; natural sources contribute about 10% of annual emissions to air. Re-emissions from soils and surface waters contribute the remainder. Re-emissions are the result of environmental accumulation of Hg from past releases to air, land and water. Given that anthropogenic emissions have been larger than natural emissions since the start of the industrial age, the bulk of re-emitted Hg is from historical anthropogenic sources. Reducing current anthropogenic emissions and releases of Hg will eventually reduce the pool of Hg that is cycling in the environment and therefore reduce future re-emissions. Estimated impacts of anthropogenic emissions reductions generally do not account for the concomitant benefit in resulting reductions of re-emitted Hg from legacy pools and, thus, understate impact of future emission controls.

One consequence of the large reservoirs of Hg already in the environment is that there is likely to be a time lag of years or perhaps decades, depending on the reservoir, before emissions reductions have a demonstrable effect on Hg levels in human food chains. This is particularly likely for Hg levels in marine food chains. This reinforces the need to continue and strengthen international efforts to reduce current Hg emissions and releases, as delays in action now will inevitably lead to slower noticeable recovery of the world's ecosystems from Hg contamination.

Substantial amounts of Hg are 'captured' during industrial operations or by air pollution control devices. Some of this Hg is recovered and enters the Hg supply or is removed to long-term storage. However, large quantities of Hg are retained in materials that are used in products, including construction materials, or disposed of in landfill. It is generally assumed that most of the Hg thus 'disposed of' is in an 'inert' form and effectively removed from the environmental Hg cycle. However, information (including measurements) regarding potential re-emissions or releases of Hg from, for example, landfills – especially uncontrolled landfills – is sparse. This issue may warrant further attention, especially in the light of possible effects of climate change on Hg (re-)cycling in the environment.

The structured databases produced to calculate the 2010 global emissions estimates and to maintain and document the data behind these estimates can provide a useful tool for investigating future emissions scenarios. The greater transparency they provide should also allow better comparisons to be made between the current inventory and future such inventories as data and methodologies are further developed and improved.

The approach used to produce the 2010 inventory estimates has a number of significant improvements on that used in the past. In addition to refining the methodology, the development of structured databases also provides greater transparency. The databases could be used in the future to continue to maintain and document data used to produce inventory estimates, and potentially to develop scenario emissions inventories. They could also provide a complement to the UNEP Toolkit when it comes to estimating and documenting trends in national emissions.

Countries also need to develop the information that is necessary to produce reliable national emission and release estimates for Hg. In this connection, the UNEP Toolkit needs to be updated and kept under continual review to incorporate new information concerning Hg content of fuels and raw materials and changes in technology that can have a major influence on emission factors and output scenarios used in calculating emissions.

The technical developments (databases and underlying data compilations, including the information compiled in Annex 6) that support the 2010 inventory are considered to be significant advances that can also be used to support future emissions inventories. No less of a development is the expert network that has been established to support the work, some elements of which could become the nuclei of future regional expert groups, for South/Central America and East Asia in particular. These networks should be maintained and further extended if at all possible.

2.5.2 Future needs/gaps in information

Improving estimates of global anthropogenic Hg emissions, and reducing uncertainties associated with these estimates requires improved information on a number of relevant subjects. Some priorities in this respect are indicted below:

- Information regarding the application of technology, both industrial processes employed and technology applied to reduce emissions of Hg (and other air pollutants) in different industries and more importantly in different countries.
- Information regarding changes in fuels used in some emission sectors, including sources and characteristics of coal burned in power generation, and alternative fuels (including co-incinerated wastes) used in the cement industry needs to be updated in order to provide robust estimates for emissions from these sectors.
- Measurement data from areas of ASGM activities. The high Hg emissions and releases associated with ASGM are not supported at present by results from field monitoring. If high Hg releases in areas where ASGM is practised are confirmed by observational and measurement data, this would increase the level of confiidence in the assumptions regarding Hg emissions and releases from this sector; however such monitoring is currently lacking.
- Information to fill gaps that would allow estimates to be made for potentially important sectors not yet included in the global inventory. These include emissions from use of Hg in VCM production, emissions from secondary metals production and ferro-alloys, oil and gas extraction, transport and processing other than refinery emissions, production and combustion of biofuels, emissions from industrial and some hazardous waste incineration and disposal, emissions from sewage sludge incineration, emissions during preparation of dental amalgam fillings and disposal of removed fillings containing Hg.
- An explanation for the relatively high emissions from secondary ferrous metal production in some countries relative to primary metal production warrants further investigation.
- Improved access to information. Some important information that could assist in further improving estimates and reducing uncertainties is not currently publicly available. This includes information on Hg content of ores and concentrates used in non-ferrous metal production, and additional information regarding Hg sources and fate in the oil and gas sector. Improved cooperation with organisations that have access to such information, including industry sources, could help meet some of these needs.
- Work to allow emissions estimates compiled and reported under different reporting systems (including national release inventories) to be reliably compared, or at least to identify the main areas that currently prevent such comparisons. This work would be essential if future (UNEP) reporting systems are to make use of existing national and other reporting systems.

3. Atmospheric Pathways, Transport and Fate

Authors: Nicola Pirrone, Sergio Cinnirella, Ashu Dastoor, Ralf Ebinghaus, Lynne Gratz, Ian Hedgecock, Francesca Sprovieri, Oleg Travnikov

Contributing authors: Elke Bieber, Richard Derwent, Xinbin Feng, Dan Jaffe, Gerard S. Jennings, Hans Kock, Alistar J. Manning, Eric Prestbo, Maik Schuetze, Andreas Schwerin, Gerard T. Spain, Andreas Weigelt

3.1 Introduction

The aim of this chapter is to provide an up-to-date overview of the major processes and mechanisms affecting the dynamics of mercury in the atmosphere and at the interfaces with other ecosystems. Understanding of Hg transformations in the atmosphere and major removal processes are dealt with in Section 3.2. Sections 3.3, 3.4 and 3.5 detail the measurements that have been made and compile the available information. The results of current modelling efforts towards an understanding of atmospheric processes at regional and global scales are detailed in Sections 3.6 and 3.7. The chapter concludes with a list of new findings on atmospheric pathways, transport and fate and an overview of research gaps and areas for future studies (Section 3.8).

Specifically, this chapter highlights recent key findings on:

- Major chemical transformations that may influence Hg transport and deposition to and/or evasion from aquatic and terrestrial ecosystems.
- Spatial and temporal variations in Hg and its compounds at ground-based sites, at different altitudes and latitudes, with reference to existing monitoring network programmes at national, regional and global scales.
- Recent advances in monitoring and analytical techniques currently used to measure Hg and its species in the atmosphere.
- Regional and global-scale atmospheric Hg models adopted to assess spatial and temporal distributions of Hg in ambient air and deposition to aquatic and terrestrial receptors for different emission scenarios.

3.2 Atmospheric chemistry

3.2.1 Speciation of emissions

Gaseous elemental mercury (GEM) is by far the most common form of Hg in the atmosphere. This is in part because the major component of anthropogenic Hg emissions is GEM, and also because natural Hg emissions (from terrestrial and oceanic surfaces) are almost exclusively GEM. A further reason for the predominance of GEM over other Hg species in the atmosphere is that GEM reacts relatively slowly with common atmospheric oxidants such as ozone (O_3), and although it reacts faster with radicals such as OH and Br (or BrO) the concentrations of these in the troposphere are so low that GEM has an atmospheric lifetime of several months to a year. This is not to say that the oxidation of GEM is unimportant in the atmosphere; however, the physical properties of GEM and in particular its volatility mean that very little if any GEM is deposited to the earth's surface. Mercury deposition to terrestrial and marine ecosystems is dominated by oxidised Hg compounds (gaseous oxidised mercury, GOM; or oxidised Hg attached to particles), both via the direct deposition of gas phase species and through wet deposition of oxidised Hg compounds in precipitation.

3.2.2 Atmospheric oxidation and reduction

Mercury can undergo oxidation in the atmosphere both in the gas and aqueous phases. In the gas phase the most important oxidants are believed to be O_3, OH and Br/BrO, while in the aqueous phase they are O_3 and OH, the concentrations of Br compounds in the atmospheric aqueous phase (cloud and rain droplets) are extremely low. Sea salt aerosol has higher concentrations of halogen compounds, however their total volume is very small compared to cloud droplets. The expression, 'are believed', has been used above quite deliberately because there is still some debate over which oxidant is the most important and even whether the compounds listed above really do oxidise Hg under atmospheric conditions. A debate over which compounds oxidise GEM in the atmosphere has been underway for a number of years; between 2006 and 2008 a series of articles entitled 'Scientific uncertainties in atmospheric mercury models' was published (Lin et al., 2006, 2007; Pongprueksa et al., 2008), the subject was reviewed again in 2009 (see Ariya et al., 2009 and Hynes et al., 2009), and a two part review has recently been published entitled 'A review of the sources of uncertainties in atmospheric mercury modelling' (Subir et al., 2011, 2012). Because the current methods used to detect GOM[9] compounds in the atmosphere require the reduction of GOM to GEM to allow detection at the very low concentrations found in the atmosphere, there is no experimental evidence of precisely which Hg compounds are comprised in the total GOM.

Global, regional and box modelling studies have been used recently in an attempt to constrain the oxidation rate of GEM in the atmosphere by comparison with observations. Holmes et al. (2010a) investigated the possibility that Br-containing compounds were the sole atmospheric oxidants of GEM using a global model, and found that their results were compatible with observations. Sprovieri et al. (2010) used GOM and GEM data obtained in the Mediterranean marine boundary layer (MBL) to examine the capacity of published

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[9] During the last five years the term GOM (Gaseous Oxidized Mercury) has replaced RGM (Reactive Gaseous Mercury).

rate constants for the reactions of GOM with O_3, OH or Br compounds to account for the observations. Hedgecock et al. (2008) used a box model to assess the published GEM + Br rate constant values with measurements of GEM and GOM obtained during an atmospheric mercury depletion event. The atmospheric lifetime of GEM in the atmosphere has come under scrutiny owing to the possibility that Br is the major atmospheric oxidant of GEM. A modelling study by Hedgecock and Pirrone (2004) suggested that as a result of the release of reactive halogen-containing compounds from sea salt aerosol in the MBL the cycling of Hg over the oceans could be rapid, and the lifetime of GEM of the order of days under certain conditions. The reduction of deposited GOM and the re-emission of GEM from the sea surface would maintain the relatively constant GEM concentration. Holmes et al. (2009) also found a lifetime of a number of days in the MBL in their modelling study and suggested that the major sink for GOM was scavenging and subsequent deposition of the marine aerosol. Recently, Obrist et al. (2011) observed some of the highest measured concentrations of GOM near the Dead Sea, they provide compelling evidence that the GEM oxidants responsible are Br-containing compounds, and at high temperatures. It is now clear that GEM oxidation by Br-containing compounds is occurring at all latitudes, and not just at the low temperatures found in the Arctic as Obrist et al. (2011) observed GEM oxidation at temperatures up to 45 °C in the Dead Sea region.

These studies indicate that Br and Br-containing compounds are valid possibilities for the role of major atmospheric GEM oxidant. A large number of models continue to use O_3/OH as the atmospheric oxidants of GOM, not least because the sources and fate of atmospheric Br-containing compounds is not well known.

Gaseous oxidised mercury can be reduced in the atmosphere, and it is believed that this occurs mostly in the aqueous phase via the decomposition of $HgSO_3$, or as has been suggested, via a two-step mechanism involving HO_2 (for all HgII compounds), although the possibility that the HgI intermediate formed is very rapidly re-oxidised by dissolved O_2 has led some authors to doubt the validity of the mechanism under typical atmospheric conditions. It is known that $Hg(OH)_2$ is reduced photolytically to GEM, however this reaction is too slow to be of atmospheric importance (Gårdfeldt and Jonsson, 2003).

Recently, due to a combination of the ever increasing number of monitoring initiatives, field studies and modelling investigations it has become possible to gain an insight into the balance between Hg oxidation and reduction in the atmosphere. This has led some authors to suggest that there may be gas phase reduction reactions occurring in the atmosphere. One suggestion that was made but which is difficult to demonstrate or infer from data is the reaction between GOM and CO (Pongprueksa et al., 2008). Another suggestion which has gained prevalence over recent years and which appears to be supported by experimental evidence is that Hg can be reduced by SO_2 in the atmosphere. Some observations suggest that the proportion of GOM to GEM downwind of large industrial installations, in particular coal-fired power plants, is – in some cases – not as high as would be expected from measurements performed at the stack. This has led some authors to suggest that the concentrations of SO_2 in these plumes are high enough to reduce an appreciable fraction of the GOM originally present at the exit of the stack (Lohman et al., 2006). This hypothesis has recently been tested using modelling studies in which the ratio of GOM to GEM in the power plant plumes is reduced (Zhang et al., 2012a). Zhang et al. (2012a) in fact found that their modelling results matched the observations more closely if the GOM content of the plume was lower. This effect has however not been observed in other studies where the power plant plumes have been the focus of the study, such as those by Kolker et al. (2010) and Gustin et al. (2012). The gas phase reaction of Hg + SO_2 has never been observed in the laboratory and has been inferred from observations and modelling only, but it is a good example of the uncertainty which still surrounds the question of atmospheric Hg oxidation and reduction.

The questions still unanswered concerning the oxidation of GEM do not stop with the incomplete knowledge of the oxidants and rates of reaction. When GEM is oxidised the products of the oxidation process are not known, in fact whether the products are in the gas or solid phase is still under debate. The reviews cited previously and a recent study by Amos et al. (2012) give an idea of the problems involved, which as previously mentioned derives at least partly from the current techniques used to sample and subsequently detect oxidised Hg compounds.

3.2.3 Mercury at environmental interfaces

There are several processes which occur at ecosystem and phase interfaces which can oxidise or reduce Hg. They occur at the interfaces between the atmosphere and lake, ocean (marine), snow, soil, vegetation and atmospheric aerosol surfaces, mostly as a result of photolytic processes, although thermal and biological processes also play a role. These reactions are often followed or accompanied by the exchange of Hg from one environmental compartment to another. For instance GOM which is reduced (probably) by sunlight in the surface layer of the ocean is usually subsequently emitted to the atmosphere as GEM. However, in most instances the details of the chemico-physical processes occurring are poorly understood and difficult to quantify.

One example of rapid Hg deposition and re-emission is the phenomenon known as an 'atmospheric mercury depletion event' (AMDE). These events occur in polar regions around the polar dawn during which significant amounts of reactive Br-containing compounds are released to the atmosphere. These compounds react with both O_3 and GEM and can locally decrease their concentrations to below the instrumental detection limits. This phenomenon has been studied in several polar regions by a number of research teams over the last ten to fifteen years, the possible impact of a significant flux of Hg to a pristine and fragile ecosystem having caused concern when it was discovered. However it seems that although the deposition flux of GOM can be high over short periods, a large fraction if not all of the GOM deposited to the snow surface is subsequently re-released to the atmosphere, as GEM, after being photolytically reduced.

The oxidation, deposition, reduction and re-emission of Hg during AMDEs is probably the most studied of the atmosphere/surface interactions involving Hg, and although the oxidation and deposition component is mostly understood, the processes involved in reduction and re-emission are less clear. See Chapters 14 (Hynes et al., 2009) and 15 (Ariya et al., 2009) of the technical report of the UNEP-MFTP (Pirrone and Mason, 2009), and Subir et al. (2012) for a more detailed discussion of the current understanding of Hg chemistry at atmospheric interfaces.

3.2.4 Overview of atmospheric mercury dynamics

It is impossible to understand the redistribution of atmospheric Hg emissions and their subsequent deposition around the globe without recourse to modelling tools and studies. Although it is possible to measure emissions at Hg sources, and Hg species concentrations in the air almost anywhere in the world (although this has not happened so far), the link between sources, measured concentration fields and measured deposition fluxes can only be clarified using chemical transport models that simulate the chemistry and dynamics of the atmosphere. Because the speciation of atmospheric Hg is the determining factor for its atmospheric lifetime, when modelling the transport and deposition of Hg it is necessary to have a good understanding of the nature of Hg emissions. It is equally important that the chemistry of the atmosphere is accurately represented in terms of the potential oxidants of Hg. As discussed later in this chapter atmospheric Hg models are generally divided into two categories by scale, either global or regional, where regional could however cover scales as large as the North American continent, Europe or the Mediterranean Basin, for example. Global scale models are required because of the lifetime of atmospheric GEM, which is transported between continents, but which necessarily use a relatively coarse resolution. They are nonetheless capable of identifying major atmospheric transport pathways. A number of studies have investigated the sources of Hg in the Arctic, identifying in particular Europe and North America as the most important source regions, and establishing their relative importance at different times of the year and as a function of major climatological indices (such as the North Atlantic Oscillation) which influence atmospheric transport on very large scales. The outflow of atmospheric pollution in general from southern and South-East Asia has also been studied and modelling and experimental studies have shown that transport from these regions influences GEM concentrations on the U.S. west coast. Transport from the U.S. east coast has been shown to influence pollutant levels (including Hg) over Western Europe.

Regional models on the other hand employ finer spatial resolution and can be used to investigate more specific source areas, even to the point of individual industrial areas, and to assess their impact on local and regional Hg deposition. It should be reiterated that knowledge of the speciation of Hg emissions is of paramount importance in these studies. In particular, the ratio of GOM to GEM will have a major impact on deposition within a radius defined by a few days dispersion, clearly local meteorology plays an important role, in the eventual deposition distribution. There has been some discussion recently not only of the speciation of emissions but also of the influence that 'in-plume' chemistry may have on the effective emissions from a given source, see Section 3.2.1.

Recently it has been acknowledged by the atmospheric Hg modelling community that it is not feasible to use regional models without input from global models. The transport from southern Asia to the U.S. west coast, from North America to Europe and from almost everywhere in the northern hemisphere to the Arctic at some time of the year, mean that knowledge of how the Hg species concentrations change in space and time at the boundaries of the regional modelling domain is crucial to the success of the study. However, combining global model output with a regional model can lead to inconsistencies. All models use parameterisations to describe the various aspects of atmospheric physics and chemistry, and if they are dissimilar between the global and regional models this can lead to inconsistent results. A model intercomparison using three different global and three regional models was performed by Bullock et al. (2009) who demonstrated the importance of the boundary conditions in regional simulations and showed this to be true for a region as large as the continental United States.

One of the biggest difficulties faced when modelling the emission transport and deposition of Hg, besides the uncertainty in the atmospheric chemistry of Hg, and the difficulties inherent in modelling atmospheric dynamics is the lack of measurement data with which to compare results. There is a particular lack of long-term monitoring data; there are very few places where GOM is monitored, and the southern hemisphere has almost no monitoring data at all. However, this situation has begun to change in the last year or so due to the GMOS (Global Mercury Observation System) project, which should enable models to be refined. With greater confidence in model performance it will be possible to begin investigating the changes in atmospheric Hg cycling which may occur under a changing climate, and to assess with more confidence the consequences of global and regional emission reductions on Hg deposition fluxes.

Only in the last four or five years has there been much progress in the multi-compartment modelling of Hg. While this is not strictly 'atmospheric mercury chemistry', the advances made in linking atmospheric to ocean and terrestrial models is important in understanding the atmospheric Hg cycle, and very importantly, these models are beginning to identify the links between atmospheric Hg deposition and the impact of Hg on the environment, that is, MeHg in the food web. Previously, multi-compartment models estimated the loadings of Hg in environmental compartments, the rate of exchange of Hg between them and attempted to balance the global Hg budget. These models are now becoming more complex and while still using parameterisations for a number of processes, they combine dynamic descriptions of the atmosphere, the upper part of the ocean and parts of the lithosphere (Selin et al., 2008; Sunderland et al., 2009; Smith-Downey et al., 2010). There is mounting evidence to support the idea that much of the MeHg found in biota has its origin in the *in situ* methylation of Hg in the water column, and the most important source of Hg to the world oceans is deposition from the atmosphere. It has been suggested that there is possibly a linear relationship between the inorganic Hg concentration in the ocean and the amount of MeHg formed in the upper waters of the ocean (Mason et al., 2012). For a more detailed discussion, see Chapter 5. Atmospheric deposition of Hg to the oceans (and land) depends on atmospheric Hg oxidation. Hence the need for more atmospheric Hg monitoring and more laboratory studies in order to elucidate the processes occurring in the atmosphere.

3.3 Monitoring networks and programmes around the world

In the past two decades, coordinated monitoring networks and long-term monitoring sites have been established in a number of regions and countries for the measurement of Hg in ambient air and wet deposition. Both Europe and North America have multiple sites with high quality continuous monitoring of Hg in air and wet deposition for more than 15 years. In addition, the High Arctic has been an area of active, continuous Hg monitoring. Notable areas with shorter, yet also high quality continuous Hg air monitoring sites can be found in the East Asian countries and South Africa. Regions with few or no records of high quality, continuous Hg monitoring sites include southern Asia, Africa, South America and Australia. International efforts are now underway to establish long-term monitoring sites with expanded global coverage.

Monitoring of ambient air Hg is focused on the three primary forms of Hg in the atmosphere: GEM, GOM, and particulate bound mercury ($PBM_{2.5}$, particle diameter <2.5 µm). The concentration of Hg and Hg compounds in ambient air is in the parts per quadrillion range, by volume (ppqv). Typically the range is reported in the literature as 0.01–10 ng/m^3 (~1–1000 ppqv). The measurement of atmospheric GEM is routine, robust and can be easily implemented due to its relatively high concentration and chemical stability. In contrast, measurements of the atmospheric Hg species GOM and $PBM_{2.5}$ are more challenging and uncertain due to their extremely low concentrations and chemical instability. Although average GOM and $PBM_{2.5}$ concentrations are commonly <1 ppqv (<10 pg/m^3), these trace species are integral to the processing of atmospheric Hg, and therefore measurements of GOM and $PBM_{2.5}$ are critical to help define and model the fate and transport of atmospheric Hg.

The low concentration of Hg in ambient air has lead research and monitoring networks to choose gold-trap pre-concentration and cold vapour atomic fluorescence spectroscopy (CVAFS) detection as the dominant measurement technique (Ebinghaus et al., 2009). The use of cold vapour atomic absorption spectroscopy (CVAAS) is an alternative measurement technique for GEM; however, because it is less sensitive and more prone to interferences, CVAAS is suitable for the higher air Hg concentrations that may occur in or near contaminated industrial sites. The automated, continuous gold-trap CVAFS method for GEM was first used in 1993 (Schroeder et al., 1995), and is by far the dominant choice for measuring Hg in ambient air (Valente et al., 2007). The automated method for continuously measuring GEM, GOM and $PBM_{2.5}$ is described by Landis et al. (2002). Although there are numerous quality assurance measurements that can be made with GEM standards to quantify precision and accuracy, a major limitation is the lack of a standard reference source for calibration of GOM or $PBM_{2.5}$ measurements at ambient air concentrations. Recent research has suggested for the first time that measured speciation ratios may be biased due to the potential for a variable fraction of collected GOM converting to GEM when ozone levels are elevated (Lyman et al., 2010). For measurements in the free troposphere where both ozone and GOM can be highly elevated, an alternative GOM collection method was used (Swartzendruber et al., 2006; Lyman and Jaffe, 2012). Additionally, the current measurement techniques for GOM and $PBM_{2.5}$ do not identify the specific chemical forms of oxidised Hg, and this is a significant gap in the current understanding of atmospheric Hg chemistry as well as an area of ongoing research.

Mercury wet deposition is one of the most useful measurements of Hg that can be made to evaluate Hg input to sensitive ecosystems and monitor long-term trends. With proper trace-metal clean techniques, a high quality laboratory and relatively inexpensive equipment, wet-deposition of Hg can be measured routinely. Experts have demonstrated that four key components are required for accurate Hg wet deposition measurements: (i) a trace-clean sample train with an HCl preservative in the collection bottle, (ii) a temperature-controlled collector with an automated rain sensor, (iii) a rain gauge to verify the rainfall depth collected, and (iv) a CVAFS system to measure the Hg concentration (Vermette et al., 1995; Landis and Keeler, 1997; Mason et al., 2000; Lindberg et al., 2007). In addition, manual event-based Hg wet-deposition sampling, which requires the presence of an operator to install and/or uncover the sample train for individual precipitation events, is also a possible technique for use in intensive studies (Dvonch et al., 1998; White et al., 2009). Both the U.S. EPA and the European Committee for Standardization (CEN) have developed standard methods for quantifying Hg in water samples (the U.S. EPA Method 1631 Revision E for determination of Hg in water samples, and the CEN EN ISO 17852 for determination of Hg wet deposition).

Tables 3.1 and 3.2 provide a summary of the existing networks for ambient air Hg and Hg wet deposition, respectively.

3.3.1 Europe

The European Monitoring and Evaluation Programme (EMEP) was one of the first international environmental measurement networks established in Europe. Over the past 40 years, a number of atmospheric measurements, such as sulphur, nitrogen compounds, and ozone, have been made across 11 countries in Europe. In more recent years, EMEP has also expanded to include heavy metals, Hg, and some persistent organic pollutants (POPs). Heavy metals were officially included in the EMEP monitoring programme beginning in 1999. Several countries have also been measuring and reporting on heavy metals within the EMEP area in connection with different national and international programmes such as the Arctic Monitoring and Assessment Programme (AMAP), the Helsinki Commission (HELCOM, the governing body for the Convention on the Protection of the Marine Environment of the Baltic Sea Area), the OSPAR Commission (the governing body for the Convention for the Protection of the Marine Environment of the North-East

Table 3.1 Monitoring networks worldwide for measurements of mercury in ambient air.

Location	Programme	Region	Duration	Measurements	Source	Website
Europe	EMEP	Continental	From 1985	Automated and manual TGM[a]	Wängberg et al., 2007	www.emep.int
USA/Canada	NADP-AMNet	National	From 2009	Automated speciation	Prestbo et al., 2011	http://nadp.isws.illinois.edu/amn/
Canada	CAMNet	National	1996–2007	Automated TGM	Kellerhals et al., 2003; Steffen et al., 2005; Temme et al., 2007; Cole and Steffen, 2010; Cole et al., 2012	
	CAPMoN	National	From 2007	Automated TGM		www.ec.gc.ca/rs-mn
	CARA	National	From 2005	Automated speciation		
USA	UMAQL	Midwest	1999–2009	Manual TGM and $PBM_{2.5}$; Automated speciation	Landis et al., 2002; Lynam and Keeler, 2005, 2006; Liu et al., 2007, 2010; Gratz et al., 2013a	
Polar Regions	AMAP	Arctic Circle	From 1991	Automated TGM		www.amap.no
Global	GMOS	Global	From 2011	Automated TGM/GEM and Automated speciation	Sprovieri et al., 2012	www.gmos.eu

[a] TGM represent the total concentration of all forms of gaseous mercury compounds in ambient air. GEM: is the gaseous elemental mercury measured by removing the oxidized compounds by means of KCl coated denuders and particle-bound mercury by the sampling air stream. (Landis et al. 2002).

Table 3.2 Monitoring networks worldwide for measurements of mercury in wet deposition.

Location	Programme	Region	Duration	Measurements	Source	Website
Europe	EMEP	Continental	From 1987	Weekly to monthly; bulk and wet-only collection	Wängberg et al., 2007	www.emep.int
USA	NADP-MDN	National	From 1996	Weekly; wet-only collection	Butler et al., 2008; Prestbo and Gay, 2009; Risch et al., 2012	http://nadp.isws.illinois.edu/MDN/
	UMAQL	Midwest and Northeast	From 1992	Daily-event; wet-only collection	Burke et al., 1995; Landis et al., 2002; Keeler and Dvonch, 2005; Keeler et al., 2006; White et al., 2009; Gratz et al., 2009, 2013b; Gratz and Keeler, 2011	
	UMAQL	Florida	1995 2008–2010	Daily-event; wet-only collection	Dvonch et al., 1998, 1999, 2012	
Canada	CAMNet/ CAPMoN	National	From 1996	Weekly; wet-only collection	Prestbo and Gay, 2009; Risch et al., 2012	www.ec.gc.ca/rs-mn
Global	GMOS	Global	From 2011	Weekly; wet-only and bulk collection	Sprovieri et al., 2012	www.gmos.eu

Atlantic), the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization (WMO), and the United Nations Framework Convention on Climate Change. EMEP continues to interact with and make use of research activities performed by the scientific community, particularly through the establishment of 'supersites' within other concurrent monitoring programmes.

The EMEP monitoring stations, however, are not uniformly distributed throughout Europe. Most sites are located in the northern, western and central parts of Europe, while only a few sites measure heavy metals in the southern and eastern parts of Europe. Mercury measurement data from EMEP are largely available only from north and northwest Europe. In 2003, 23 sites were measuring heavy metals in both air and precipitation, and 15 sites were measuring at least one form of Hg. The locations of the Hg measurement sites within the EMEP network are shown in Figure 3.1.

A particularly interesting and important Hg monitoring site within EMEP is the Mace Head site, which maintains the longest time series of atmospheric Hg measurements with high time resolution in the temperate marine background atmosphere. Mace Head is located on the west coast of Ireland (53°20'N; 9°54'W) and is exposed to the North Atlantic Ocean. TGM measurements using a Tekran Hg analyser (Model 2537A) (Ebinghaus at al., 2011) began in September 1995. Meteorological records indicate that about 50% of the air masses arriving at Mace Head are within the clean sector and have recently traversed the thousands of kilometres of uninterrupted fetch across the North Atlantic Ocean. There is no industrial activity that might influence measurements at the station within about 90 km of the site. TGM baseline measurements are considered representative of the unpolluted northern hemisphere and have been used to determine trends in TGM concentrations over the period 1995–2009 (Ebinghaus et al., 2011; see Section 3.4.1 for details).

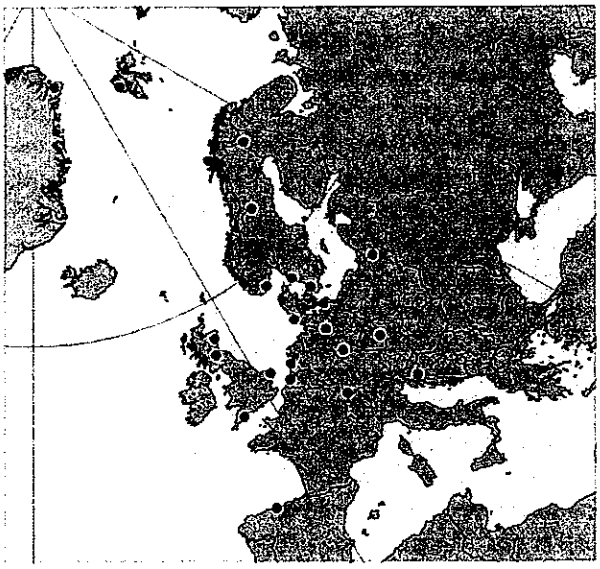


Figure 3.1 Mercury measurement sites within the EMEP network. Source: after Travnikov et al. (2012).

3.3.2 North America (USA and Canada)

3.3.2.1 Ambient mercury

In Canada, measurements of ambient air Hg and Hg wet deposition have been carried out through a series of monitoring networks led by Environment Canada, including the Canadian Air and Precipitation Monitoring Network (CAPMoN), the Canadian Atmospheric Monitoring Network (CAMNet), the Northern Contaminants Program (NCP), and the Canadian Clean Air Regulatory Agency (CARA). CAMNet began monitoring TGM at sites across Canada in 1996, and as of 2007 these measurements are conducted under the auspices of CAPMoN. There are currently four CAPMoN sites for continuous measurements of TGM. The NCP and Environment Canada have also been monitoring ambient air Hg at the Dr. Neil Trivett Global Atmospheric Watch Observatory at Alert, where measurements for GEM have been continuously measured since 1995 and speciated ambient Hg has been monitored since 2002. In 2005, the CARA Hg programme began monitoring speciated Hg at three sites in Canada, while NCP and Environment Canada added an additional site for Hg speciation. Currently, atmospheric Hg speciation is measured at four sites in total: Alert, St. Anicet, Kejimikujik, and the Experimental Lakes Area. Figure 3.2 shows the past and current atmospheric Hg monitoring at sites across Canada. A detailed analysis of all atmospheric Hg measurements in Canada is expected in the forthcoming Canadian Mercury Science Assessment, due out in 2013.

In the United States, a number of research-based individual monitoring sites and local/regional networks have existed over the years for measuring ambient air Hg. Recently, the Atmospheric Mercury Network (AMNet) was created within

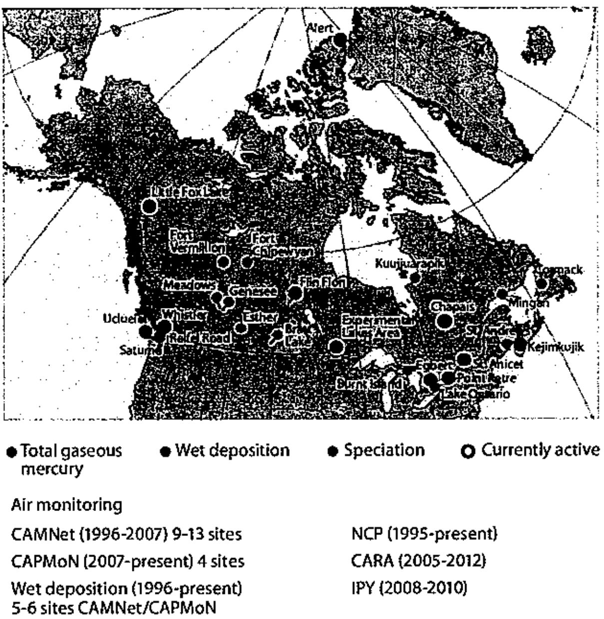


Figure 3.2 Locations of the past and current atmospheric mercury monitoring sites and networks across Canada. Source: Environment Canada.

the National Atmospheric Deposition Program (NADP) with the support of various U.S. government agencies and academic research communities, and in coordination with Canadian monitoring programmes. NADP and its partners launched AMNet by integrating several existing speciated Hg monitoring sites across the U.S. and Canada under a common framework. New monitoring sites were added to AMNet, as resources permitted. The network currently includes 21 sites where measurements of GEM, GOM and PBM$_{2.5}$ are made using the Tekran Hg speciation system (Sharac et al., 2011). AMNet was established for the purpose of measuring atmospheric Hg fractions, which contribute to dry and total Hg deposition. Sites measure concentrations of atmospheric Hg species from automated, continuous measuring systems, concentrations of total Hg in precipitation, and meteorological measurements, when available locally. Included in AMNet is a high-altitude site representative of background concentrations at Mauna Loa, Hawaii (discussed further in Section 3.5.1). Data from this site are available to the global community. In 2009, AMNet was formally recognised as a national network within the NADP and data products are available to anyone via their website (Figure 3.3). A significant contribution of AMNet has been the development of standard operating procedures (SOPs) for equipment operation and data management. The SOPs were developed with input and review from the majority of the atmospheric Hg monitoring experts from around the world. These SOPs have been a template for other network SOPs, such as the Global Mercury Observation System (GMOS) and also individual monitoring sites throughout the world, thus providing a common basis for data comparison.

While the Canadian CAMNet preceded AMNet in the development of SOPs for equipment operation and data management, it was imperative that both countries' ambient air Hg monitoring networks have equivalent quality assurance and quality control programmes and techniques for atmospheric Hg speciation data (Steffen et al., 2012). Efforts such as this will help to ensure that atmospheric Hg measurements collected on a network-scale are highly comparable and applicable to the modelling and policy communities.

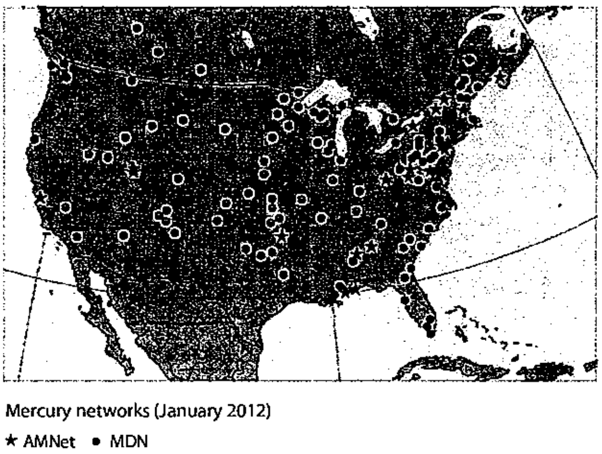


Figure 3.3 NADP Mercury Deposition Network Sites (MDN, http://nadp.isws.illinois.edu/MDN/) and NADP Air Mercury Network Sites AMNet ambient air mercury speciation sites (http://nadp.isws.illinois.edu/amn/). Source: National Atmospheric Deposition Program and Prestbo et al. (2011).

3.3.2.2 Mercury in precipitation

Long-term measurements of Hg wet deposition in the United States and Canada largely commenced in the mid-1990s following the Clean Air Act Amendments of 1990, which mandated monitoring of several hazardous air pollutants, including Hg. A number of monitoring sites were established (Figure 3.3), several of which are still operational today, producing nearly two decades of Hg wet-deposition records. In the Great Waters region, which includes the Great Lakes, Chesapeake Bay, and Lake Champlain basins, monitoring sites in Dexter (Michigan) and Underhill (Vermont) began in 1992 under the supervision of the University of Michigan Air Quality Laboratory (UMAQL). Additional sites were added in Pellston and Eagle Harbour (both in Michigan) in 1993, creating the foundations for the Michigan Mercury Monitoring Network that expanded over time to include other sites in Michigan, Ohio, and Illinois (Keeler and Dvonch, 2005; Keeler et al., 2006; Gratz et al., 2009; 2013b; White et al., 2009).

The NADP's Mercury Deposition Network (MDN) formed in 1996 and has grown to include more than 100 monitoring sites nationwide. The MDN programme (Figure 3.3) has also worked closely with the Canadian monitoring programmes, including CAMNet and CAPMoN, to develop consistent sample collection and analysis procedures. All precipitation samples from both the MDN and CAPMoN programmes are analysed at a common laboratory in the United States (Frontier Global Sciences) to ensure consistent analytical results. In more recent years, new sites have also been established in Mexico. As a result, the U.S. and Canadian monitoring networks have generated a long-term record of Hg wet deposition throughout North America over the past 20 years.

3.3.3 Asia

For nearly a decade, independent programmes and networks for monitoring atmospheric Hg species and deposition have been developed in Asia, such as those in Korea, Japan, China, and Taiwan. Most of the early measurements in this area were financially supported by the National Science Foundation in each of the Asian countries. A pilot project for monitoring atmospheric Hg started in 2007 at the Cape Hedo site on Okinawa Island of Japan (Suzuki et al., 2009), where continuous measurements began with TGM only and now include continuous measurements of GOM and PBM$_{2.5}$ (Japan Ministry of the Environment, 2012). Since the establishment of the GMOS project, many of these sites have been incorporated into GMOS (Sprovieri et al., 2012). At present, there are nine ground-based monitoring sites in Asia involved in the GMOS monitoring network. Of the nine GMOS sites in Asia, four ground-based sites including Mt. Waliguan baseline observatory, Mt. Changbai station, Mt. Aishao station and Mt. Lulin Atmospheric Background station are located in China, and respectively represent the background monitoring of atmospheric Hg species and wet deposition in the northwest, northeast, and southwest of China and Taiwan. Two sites in Japan, located in Cape Hedo (Okinawa Island) and Minamata (Kyushu Island), were also selected as GMOS ground-based sites. The GMOS monitoring sites in Korea and India are located in Kanghwa Island (northwestern Korea) and Kodaikanal (southern India), respectively. In addition, the highest-altitude site in the GMOS monitoring network, EvK2CNR, is located in the northeastern area of Nepal. These measurement sites are an important addition to the GMOS network and will improve understanding of atmospheric Hg species in this area of the world.

3.3.4 Polar regions (Arctic and Antarctica)

The Arctic Monitoring and Assessment Programme (AMAP) established in 1991, is a coordinated air monitoring programme covering the circum-Arctic areas of North America and Eurasia. The AMAP programme has an active ambient air Hg monitoring component with sites in Canada, USA, Russia, Norway and Greenland (Denmark). The Global Atmospheric Watch (GAW) site at Alert operated by Environment Canada has the longest, continuous record of GEM (17 years) and Hg speciation (10 years) in the Arctic. Continuous monitoring for long periods has also occurred at: (1) Amderma (Russia), (2) GAW Ny Alesund 'Zepplin' site (Svalbard, Norway) and (3) AMAP 'Station Nord' (Greenland-Denmark). Shorter term Arctic ambient air Hg monitoring and research has occurred at several other sites. There were no monitoring networks for atmospheric Hg species established in Antarctica before the establishment of GMOS. However, several important short-term Antarctic ambient air measurements were carried out during episodic field campaigns. The Antarctic regions have not been extensively monitored yet, and so there is little information available on spatial and temporal trends in atmospheric Hg there. Currently, the GMOS network is supporting or associated with key Arctic sites such as Zepplin (Svalbard, Norway), Station Nord (Greenland-Denmark), and Alert (Ellesmere Island, Canada). In Antarctica, the GMOS network includes the GAW French-Italian monitoring Station 'DOME-C' on the Antarctic Plateau and the GAW coastal French Research Station, 'Dumont d'Urville'.

3.3.5 GMOS

The Global Mercury Observation System (GMOS) project (www.gmos.eu) commenced in November 2010 with the goal of developing a coordinated global observation system for Hg, including a large network of ground-based monitoring stations in order to improve the global-scale coverage of atmospheric Hg measurements. The GMOS ground-based stations (see Figure 3.4) are primarily remote background monitoring sites at both high altitude and sea level locations. New sites are being developed in regions of the world where few observational data are available on atmospheric Hg. The measurements from these sites will be used to assess levels of atmospheric Hg and Hg deposition at individual monitoring sites, as well as to validate regional and global scale atmospheric Hg models. This information will improve understanding of global atmospheric Hg transport and deposition, and it will importantly contribute to future international policy development and implementation.

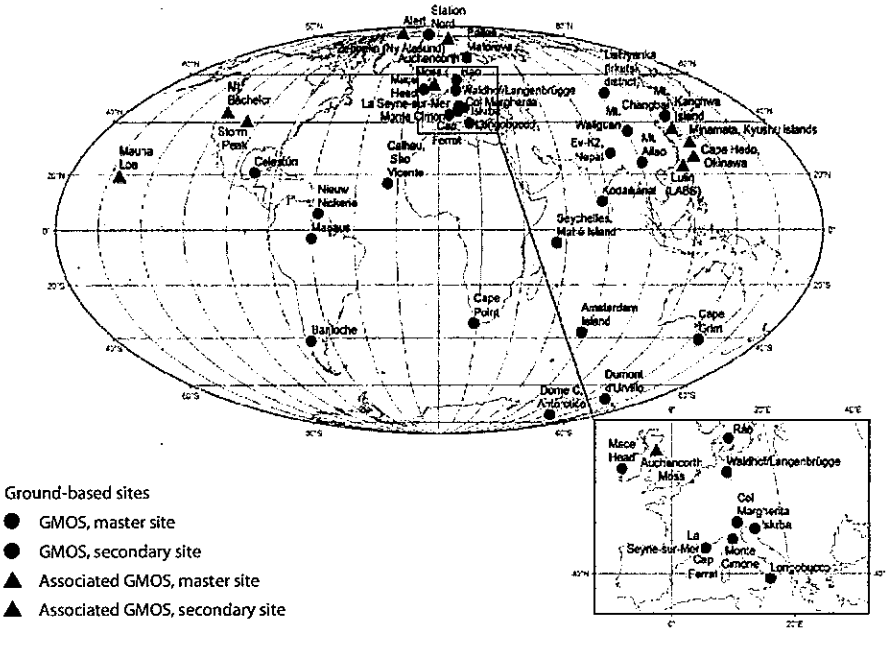


Figure 3.4 Ground-based monitoring sites participating in the GMOS programme (www.gmos.eu). GMOS Master sites are those where GEM, GOM, and $PBM_{2.5}$ are continuously measured and Hg in rainfall measured where appropriate. Secondary GMOS sites are those where only TGM and Hg in precipitation are continuously measured. Associated GMOS sites are those that are managed by external GMOS partners who have agreed to share their measurement data with the GMOS programme and measurement database.

To date, there are 38 monitoring sites participating in the GMOS network. These include existing sites that are already collecting atmospheric Hg measurements (ambient air and/or precipitation), in particular several global monitoring sites such as Mace Head (Ireland) and Cape Point (South Africa) which have been monitoring concentrations of atmospheric Hg for many years and can offer an important historical measurement record to the project (Sprovieri et al., 2012). The GMOS network also includes new background stations (with an emphasis on the southern hemisphere regions where networks did not previously exist) which are initiating Hg measurements for the first time, and externally partnering sites who are contributing their measurement data to the GMOS database.

3.4 Atmospheric mercury measurements and trends worldwide

3.4.1 Ambient atmospheric mercury measurements and trends

3.4.1.1 Europe

Extensive measurements and data analysis have been performed at the Mace Head (Galway, Ireland) monitoring site for nearly two decades. Overall, a decreasing trend in TGM concentrations was observed at Mace Head from 1996 to 2011, and these findings have been an important new contribution to the scientific literature (Ebinghaus et al., 2011). To determine trends in TGM, it was important to select air masses that were representative of the unpolluted northern hemispheric marine boundary layer. At Mace Head, an atmospheric dispersion modelling method (Ryall et al., 1998) was employed to separate baseline air measurements. The modelling techniques are described in more detail by Ryall and Maryon (1998) and Ryall et al. (1998), and further refinements to the model using a back-attribution technique are described by Manning et al. (2003). As an example, Figure 3.5 shows the composite of all air mass history maps assigned to the baseline category for 1998.

Air masses, assigned to the baseline category on an hourly basis, were extracted from the complete dataset to form a baseline meteorological dataset (Ebinghaus et al., 2011). The hourly average TGM observations were then extracted from this baseline dataset to form a baseline TGM dataset for the baseline hours only. Over the 16-year period of this study, 28.6% of TGM observations were assigned to baseline air masses. Calendar month averages for TGM were then calculated for baseline air masses from the hourly values. No lower limit value was set on the number of hourly observations needed to characterise a valid monthly average. This averaged monthly baseline shows evidence of a seasonal cycle that is consistent with those observed at Mace Head for a wide variety of trace gases. It is suggested that meteorological variability is the most important factor in the establishment of the observed seasonal cycle of TGM concentrations. The presence of trends was investigated with the application of the Mann-Kendall test and Sen's slope estimate. Annual baseline TGM means decreased from 1.82 ng/m^3 in 1996 to 1.40 ng/m^3 in 2011. They showed a statistically significant negative (downward) trend of -0.027 ± 0.01 ng/m^3/y (at the 99.9% level of significance), which is 1.4–1.8% per year or 26% in the 16 years of investigation (Ebinghaus et al., 2011).

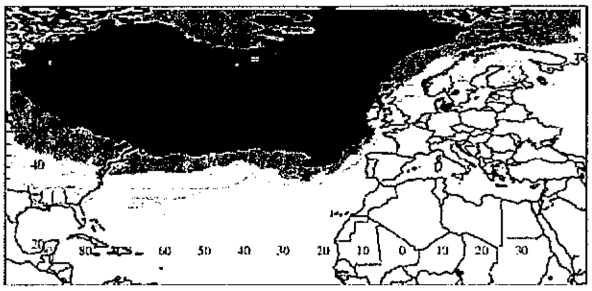


Figure 3.5 A composite of the back-attribution plots for Mace Head, Ireland for all air masses assigned to the baseline category during 1998, with the pixel shading showing the relative contribution to the air concentration at Mace Head, Ireland from the emissions of an inert tracer at that location. Source: Ebinghaus et al. (2011).

In a recent publication by Slemr et al. (2011), these observations at Mace Head were compared with similar long-term measurements at the Cape Point station in South Africa, as well as with atmospheric Hg measurements from oceanographic cruise campaigns. Cape Point has been an important monitoring site for atmospheric Hg for many years. It is a WMO-GAW station approximately 60 km south of Cape Town (Slemr et al., 2011). From 1995 to 2004, TGM was measured using manual techniques (Slemr et al., 2008), and from March 2007 to the present TGM has been measured using a Tekran automated Hg vapour analyser (Slemr et al., 2011). From 1999 to 2010, GEM concentrations decreased at Cape Point by -0.034 ± 0.005 ng/m^3/y. When cruise measurements from the southern hemisphere were included in this calculation, the observed declining trend was -0.035 ± 0.005 ng/m^3/y (Slemr et al., 2011). When a similar analysis was applied to the Mace Head annual dataset, a declining trend of -0.025 ± 0.005 ng/m^3/y was observed from 1996 to 2009, which is similar to the value reported above from Ebinghaus et al. (2011) that was obtained using baseline monthly averages (Slemr et al., 2011). These analyses provide a unique comparison of long-term trends in atmospheric Hg in the northern and southern hemispheres, and suggest that ambient TGM concentrations have declined significantly at both examined sites.

With regard to speciated atmospheric Hg measurements in Europe, since January 2009, atmospheric concentrations of GEM, GOM and PBM$_{2.5}$ have been measured continuously at the EMEP monitoring station 'Waldhof', Germany (52°48'N, 10°45'E), a rural background measurement site of the German

Federal Environment Agency (Figure 3.6). Waldhof was chosen to be one of four European GMOS master sites for continuously measuring speciated atmospheric Hg concentrations. The measurements are performed in quasi-continuous mode, using an automatic Hg analyser (Tekran model 2537A) together with a Hg speciation unit (Tekran model 1130 and Tekran model 1135). GEM is measured every five minutes, while GOM and $PBM_{2.5}$ are sampled at three-hour intervals.

Figure 3.6 illustrates the daily average concentrations for GEM (black), $PBM_{2.5}$ (red) and GOM (blue) from January 2009 to December 2011. During this three-year period, the daily median GEM concentrations varied between 1.4 and 2.0 ng/m³ (10% and 90% percentiles). The minimum and maximum daily average concentrations were 1.1 and 3.1 ng/m³, respectively. The three-year median concentration was 1.63 ng/m³, similar to the northern hemispheric background concentration of 1.7 ng/m³ (Ebinghaus et al., 2011). The median TPM concentration (6.74 pg/m³) was about five times higher than the median GOM concentration (1.27 pg/m³). $PBM_{2.5}$ and GOM showed much larger variability in daily average concentration than GEM. Based on yearly median concentrations, between 2009 and 2011 there was no trend apparent in GEM and $PBM_{2.5}$ concentrations (Table 3.3). In contrast, the yearly median GOM concentration increased by 76% from 2009 to 2010 and by 34% from 2010 to 2011. However, given the statistical limitations of the data set (three years of measurements at one site), the indicated trend will need to be verified with continuous measurements in the coming years.

Table 3.3 Yearly average concentrations (medians) for GEM, $PBM_{2.5}$ and GOM, measured at the German EMEP station and measurement site of the German Federal Environmental Agency, 'Waldhof'. Source: Weigelt et al. (2012).

Year	GEM, ng/m³	$PBM_{2.5}$, pg/m³	GOM, pg/m³
2009	1.66	7.20	0.73
2010	1.61	6.68	1.29
2011	1.61	6.42	1.72

A first seasonality analysis at Waldhof was carried out using monthly average concentrations. The most pronounced seasonal variation was observed in $PBM_{2.5}$ concentrations (Figure 3.7). During winter, the concentrations as well as the variability appear much higher than in summer. The $PM_{2.5}$ mass concentration is given in Figure 3.7 in blue, averaged for the same time periods as $PBM_{2.5}$. It is clear that $PBM_{2.5}$ concentrations show a similar seasonality as the $PM_{2.5}$ mass concentrations. Higher $PM_{2.5}$ mass concentrations in winter may reflect increased emissions in winter (e.g., from domestic heating) as well as meteorological effects (e.g., reduced height of the planetary boundary layer; Seinfeld and Pandis, 1998). Neither GEM nor $PBM_{2.5}$ show a significant diurnal cycle (not shown), whereas, a daily cycle is highly apparent for GOM (Figure 3.8). Currently it is assumed that the observed cycle is caused by local photochemical oxidation and *in situ* production of GOM.

3.4.1.2 North America

In North America, the development of national monitoring networks, regional monitoring programmes and intensive measurement campaigns has lead to the collection of various important datasets on both TGM and speciated atmospheric Hg. In Canada, the CAMNet programme's continuous monitoring of TGM has made it possible to examine temporal and spatial variability in TGM concentrations (Blanchard et al., 2002; Kellerhals et al., 2003; Temme et al., 2007). In general,

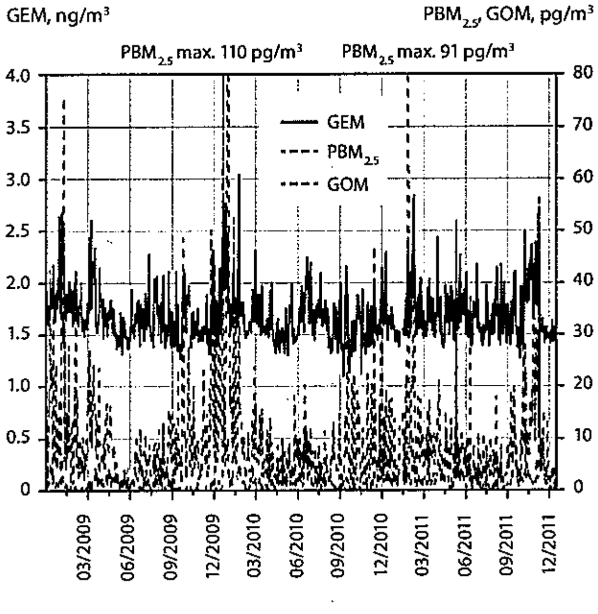


Figure 3.6 Daily averages for GEM, $PBM_{2.5}$, and GOM from January 2009 to December 2011 at the German EMEP station and measurement site 'Waldhof'. Source: Weigelt et al. (2012).

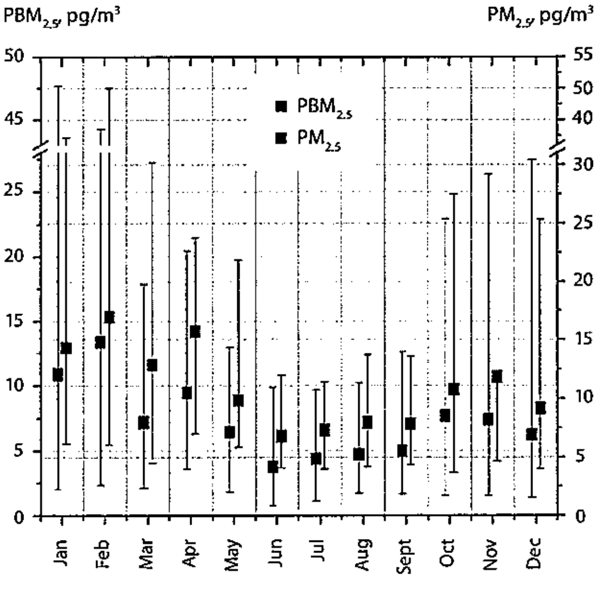


Figure 3.7 Monthly median concentration for particle bound mercury ($PBM_{2.5}$) and particle mass ($PM_{2.5}$) at the Waldhof air monitoring site, Germany (2009–2011). Source: Weigelt et al. (2012).

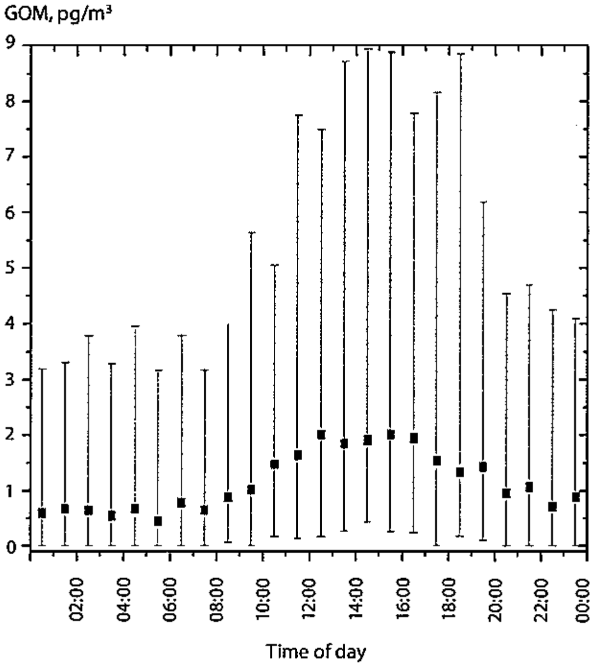


Figure 3.8 Hourly median concentration for GOM at the Waldhof air monitoring site, Germany (2009–2011). Source: Weigelt et al. (2012).

mid-latitude sites showed slightly higher TGM concentrations in late winter, and lower concentrations in summer, while diurnally the maximum concentration typically occurred near solar noon and the minimum concentration before sunrise (Kellerhals et al., 2003). It was also clear that, although the monitoring sites are in primarily rural locations, those sites that are closer to anthropogenic source regions (classified as 'rural-affected') displayed significantly higher TGM concentrations (1.70 ng/m³ on average) than rural-remote sites (1.54 ng/m³ on average) (Kellerhals et al., 2003).

Temme et al. (2007) identified a statistically significant decreasing trend in TGM concentrations at certain rural CAMNet sites from 1995 to 2005. Declines in concentration by site varied from 2.2% to 17.4%, and these findings appeared consistent with reported reductions in concentrations of Hg in precipitation at North American MDN sites (Temme et al., 2007). In addition to CAMNet, monitoring of speciated atmospheric Hg has also been carried out at selected sites in Canada (see Table 3.4).

A more recent study by Cole et al. (2012) examined 10-year trends in atmospheric TGM in the Canadian High Arctic, sub-Arctic, and mid-latitude regions. Specifically at the sub-

Table 3.4 Summary of selected studies of atmospheric TGM and speciated mercury concentrations in North America. Presented values are either reported as the mean (± SD) or a range of values depending on the specific study design and convention for data reporting in the literature.

Location	Region	Period	Measurements	TGM, ng/m³	GEM, ng/m³	$PBM_{2.5}$, pg/m³	GOM, pg/m³	Source
Canada	National (CAMNet)	1997–1999; 1995–2005	Automated TGM	1.60 ± 0.15 1.58 ± 0.17				Kellerhals et al., 2003; Temme et al., 2007
	Bay St. François	2002	Automated speciated Hg	1.40 ± 0.17	1.38 ± 0.18	6.44 ± 3.63	3.63 ± 4.07	Poissant et al., 2004
	St. Anicet, Quebec	2003	Automated speciated Hg		1.65 ± 0.42	26 ± 54	3 ± 11	Poissant et al., 2005
USA	Southern Lake Michigan (LMMBS and AEOLOS)	1994–1995	Manual TGM; manual $PBM_{2.5}$; automated TGM	(mean values) 2.1–3.6 1.7–4.1		(mean values) 12–70 6–133		Landis et al., 2002
	SE Michigan (Dexter, Detroit)	1999–2002	Automated speciated Hg		1.09–4.39 1.09–15.74	(Detroit only) 5.70–60.1	0.19–38.7 0.62–155	Lynam and Keeler, 2005
	SE Michigan (Detroit)	2003	Automated speciated Hg		2.2 ± 1.3	20.8 ± 30.0	17.7 ± 28.9	Liu et al., 2007
	SE Michigan (Dexter, Detroit)	2004	Automated speciated Hg		1.59 ± 0.59 2.47 ± 1.43	6.10 ± 5.51 18.1 ± 61.0	3.80 ± 6.62 15.5 ± 54.9	Liu et al., 2010
	New York (Potsdam, Stockton, Sterling)	2001–2002	Manual TGM; manual GOM	1.84 ± 1.24 1.83 ± 1.32 3.02 ± 2.14			4.2 ± 0.64 5.7 ± 9.2 6.0 ± 10.8	Han et al., 2004
	New York (Adirondacks)	2006–2007	Automated speciated Hg		1.4 ± 0.4	3.2 ± 3.7	1.8 ± 2.2	Choi et al., 2008
	20 AMNet Sites	2008–2009	Automated speciated Hg		(annual mean) 1.2–2.1	(annual mean) 2.9–17.1	(annual mean) 1.1–22.6	Zhang et al, 2012a

Arctic (Kuujjuarapik, Nunavik, Quebec, Canada) and mid-latitude sites (St. Anicet, Quebec, Kejimkujik, Nova Scotia and Egbert, Ontario, Canada) (Cole et al., 2012), analysis of TGM concentrations showed a decreasing trend from 1995 to 2007. The decline at the sub-Arctic Kuujjuarapik site was -2.1% per year, whereas at the mid-latitude sites the declines were -1.9%, -1.6%, and -2.2% per year for St. Anicet, Kejimkujik, and Egbert, respectively (Cole et al., 2012). These trends are in close agreement with that observed since 1996 at Mace Head, Ireland (-1.8 ± 0.2% per year) (Ebinghaus et al., 2011; see also Section 3.4.1.1).

In the United States, a number of ambient air Hg measurement campaigns have been carried out in the Midwest and the Great Lakes regions, in part because of the high density of atmospheric Hg emission sources in that area. A brief summary of the results from selected studies of ambient air Hg (both TGM and speciated Hg) in North America are presented in the Table 3.4, and references for the associated manuscripts are provided for further details. Earlier studies, such as the Lake Michigan Urban Air Toxics Study (LMUATS) (Holsen et al., 1992; Keeler, 1994), the Lake Michigan Mass Balance Study (LMMBS) (Landis et al., 2002; McCarty et al., 2004) and the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS) (Landis et al., 2002), demonstrated the important local and regional scale impacts of the Chicago/Gary urban area on TGM concentrations and levels of Hg deposition to ecosystems in the Lake Michigan Basin. Results from the LMMBS suggested that atmospheric deposition was responsible for approximately 84% of total annual Hg inputs to Lake Michigan, and that the Chicago/Gary urban area contributed approximately 20% of the annual atmospheric Hg deposition to the lake (Landis and Keeler, 2002). A more recent study using speciated ambient Hg measurements of GEM, GOM, and PBM$_{2.5}$ in Chicago (Illinois) and the downwind receptor site of Holland (Michigan) demonstrated that transport from Chicago/Gary across Lake Michigan may result in GOM concentrations at downwind receptors that are enhanced five-fold relative to transport from other directions (Gratz et al., 2013a). In specific cases of this type of transport, 50% of the elevated GOM concentrations were attributed to direct transport of primary GOM source emissions, with the remainder associated with GEM oxidation during transport (Gratz et al., 2013a). Speciated Hg measurements in the Detroit (Michigan) urban area and in the remote upwind site of Dexter (Michigan) have demonstrated the significant differences in speciated Hg between the two locations as well as the substantial local impacts that industrial emission sources can have on the levels of speciated Hg, in particular GOM, within an urban/industrial area (Lynam and Keeler, 2005, 2006; Liu et al., 2007, 2010). A study in New York state also demonstrated the elevated levels of GOM at a monitoring site near major industrial sources (Sterling), while at more remote sites (Potsdam and Stockton) GOM concentrations were noticeably lower (Han et al., 2004).

Owing to the time periods of many of these studies (of the order of a few months to one year, and in different geographic locations) it can be difficult to determine overall long-term trends in speciated Hg concentrations in the United States. However, a recent study by Mao and Talbot (2012) explored temporal patterns and trends in speciated atmospheric Hg at marine (Appledore Island), coastal (Thompson Farm), and inland (Pac Monadnock) sites in New Hampshire, USA. Analyses demonstrated decreasing trends in GEM at the coastal and inland sites of 3.3 ppqv/y over 7.5 years (2003–2010) and 6.3 ppqv/y over 5.5 years (2005–2010), respectively (Mao and Talbot, 2012). These observed declines are comparable to those reported at Mace Head, Ireland (-0.028 ± 0.01 ng/m^3/y, or -3.1 ± 1.1 ppqv/y) and at Cape Point, South Africa (-0.034 ± 0.005 ng/m^3/y, or -3.8 ± 0.6 ppqv/y). The study by Mao and Talbot (2012) represents the first attempt to explore long-term trends in atmospheric GEM at mid-latitude sites in the United States.

The Thompson Farm site is an example of one of many sites in the United States and Canada that have been in operation for several years and are now part of the NADP AMNet monitoring programme. Figure 3.9 shows the annual concentrations of

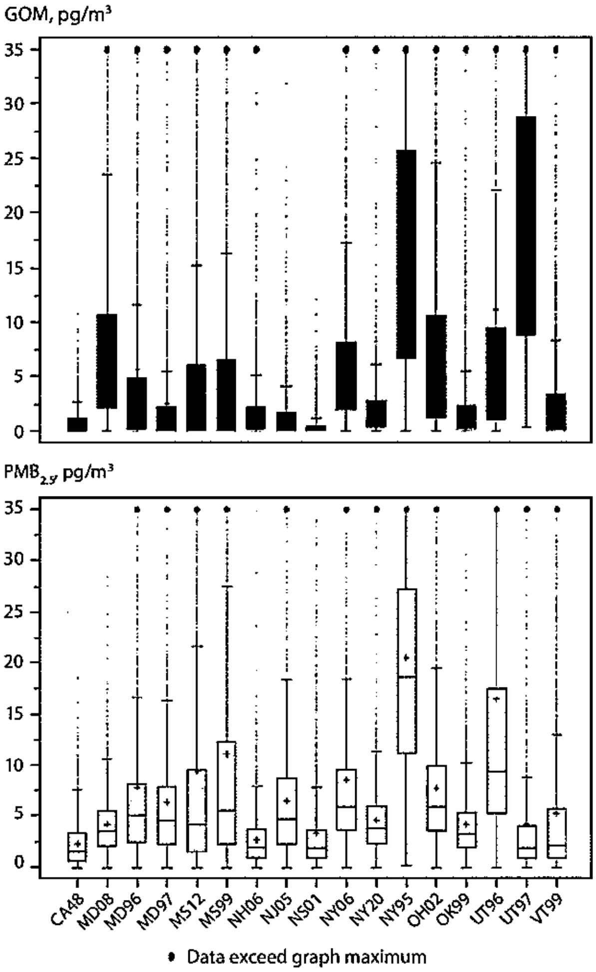


Figure 3.9 Annual GOM and PBM$_{2.5}$ observations for AMNet sites in 2010. The box whisker plots for each field site show the median (horizontal line), 70th percentile (box), 95th percentile (whisker). In general, urban and regionally impacted sites had the highest mercury speciation values, while remote coastal sites had the lowest. Source: Prestbo et al. (2011).

GOM and $PBM_{2.5}$ at AMNet sites for 2010 (Prestbo et al., 2011), demonstrating interesting variability in ambient concentrations between urban and remote sites. Zhang et al. (2012a) reported on concentrations of atmospheric Hg species across 20 AMNet sites from 2008–2009 (Table 3.4) and used the measurement dataset to estimate speciated and total Hg dry deposition. Across these sites, the annual GEM concentrations ranged from 1.2 to 2.1 ng/m³ and the highest concentrations were observed at urban and suburban locations, whereas for GOM and $PBM_{2.5}$ the annual concentrations were more variable among the sites. While the lowest concentrations of GOM and $PBM_{2.5}$ were observed at the same rural sites, the highest concentrations of GOM and $PBM_{2.5}$ were not observed at the same sites, and the observed geographical and seasonal patterns in atmospheric Hg species were attributed to several factors, including source emissions, atmospheric transport, chemical cycling, and deposition processes (Zhang et al., 2012a). As the AMNet programme continues to grow and develop, many interesting results pertaining to spatial and temporal variability in speciated ambient air Hg concentrations should become available, further informing the scientific community about the levels and long-term trends of ambient air Hg in North America.

3.4.1.3 Asia

Speciated atmospheric Hg measurements in urban and remote areas in Asia are shown in Table 3.5. Feng et al. (2004) carried out one year of continuous TGM measurements in Guiyang, south-western China. A clear seasonal pattern of TGM concentrations was observed in Guiyang, with elevated levels in cold seasons. Results indicate that TGM levels in Guiyang are much higher than in other cities around the world. Coal combustion for domestic heating and industrial activity is believed to be the major source of these elevated levels of TGM. Continuous measurements of speciated atmospheric Hg (GEM, $PBM_{2.5}$, GOM) in Guiyang were also conducted in 2009. The mean GEM, $PBM_{2.5}$ and GOM levels observed are all higher than those typically observed in urban areas of North America and Europe (Fu et al., 2011). Several short-term studies (several weeks to several months) of TGM have been undertaken in Shanghai, Ningbo (eastern China) and Chongqing (south-western China). The mean TGM concentrations recorded in Shanghai and Ningbo are much lower than those observed in Guiyang and Chongqing (mean: 6.74 ± 0.37 ng/m³, Yang et al., 2009), which is likely to be due to the exchange of clean air masses from marine areas.

In Seoul, South Korea, atmospheric Hg levels have shown a clear decreasing trend in the last decade. The concentrations in Seoul are much lower than those reported from Guiyang and Chongqing in southwest China (Fu et al., 2011). However, the mean TGM concentration in Seoul is comparable to those obtained in Shanghai and Ningbo, which are located in coastal areas of eastern China (Friedli et al., 2011; Nguyen et al., 2011).

Observations of TGM in remote areas of Asia are in the range 1.7–4.6 ng/m³, which are relatively high compared to background concentrations in the northern hemisphere (1.5–1.7 ng/m³, Lindberg et al., 2007). At the Cape Hedo Observatory in Japan, the mean GEM concentration is slightly higher than the northern hemisphere background values obtained during the observation campaign in 2004, whereas GOM and $PBM_{2.5}$ were similar to observations in North America and Europe (Valente et al., 2007). This may suggest that the export of atmospheric Hg from Asia is mainly in the form of GEM, and outflow of GOM and $PBM_{2.5}$ in the Eastern Asian boundary layer is very limited. Cape Hedo is occasionally impacted by plumes that originate from mainland China and central Japan, and this contributes to the relatively high mean TGM. In China, TGM concentrations measured in the Mt. Gongga area were significantly higher than those observed at other remote sites (Table 3.5). The elevated TGM and $PBM_{2.5}$ levels at Mt. Gongga were attributed to emissions of Hg from local domestic coal combustion and regional non-ferrous metal smelting activities (Fu et al., 2008a,b). There are no pollution control devices used during domestic burning, and the Hg emission factors for domestic coal and bio-fuel burning are likely to be significantly higher than for power plants and industrial boilers (Streets et al., 2005; Tang et al., 2007). Fu et al. (2010a) conducted a full year study of TGM at a remote site (Mt. Leigong, 2178 m a.s.l.) in Guizhou province, south-western China. This study showed a mean concentration higher than the northern hemisphere background value suggesting that this site is a frequent receptor for long-range transport of atmospheric Hg pollution from central China (e.g., Henan, Hubei, and Hunan provinces).

A one-year monitoring study of atmospheric speciated Hg was performed at Mt. Waliguan Observatory (Fu et al., 2012b). This site is one of 24 baseline WMO-GAW sites. This high altitude station (3816 m a.s.l.) on the edge of the north-eastern Qinghai-Tibetan Plateau is relatively isolated from industrial point sources and populated regions. Annual mean TGM, $PBM_{2.5}$ and GOM concentrations at this site were slightly higher than those reported from remote areas of North America and Europe (Valente et al., 2007). The speciated Hg concentrations showed a pronounced dependence on wind direction, with most of the high concentrations observed under north-easterly and easterly flow patterns. Urban areas such as Xining and Lanzhou were the most important regional source areas. In addition, long-range transport of Hg-enriched air masses from eastern Gansu, western Shanxi, western Ningxia as well as northern India also partially influenced the observations (Fu et al., 2012b).

Measurements of atmospheric TGM concentrations were also conducted in rural-affected sites in coastal areas of the Yellow Sea. The Yellow Sea is bordered by eastern China and the Korean Peninsula, which are important Hg source regions in East Asia. Most of the high-TGM events were observed close to the mainland of East China, indicating the effect of outflow of air masses from the mainland.

Table 3.5 Summary of speciated atmospheric mercury concentrations observed in Asia.

Location	Classification	Period	Method	TGM, ng/m^3	PBM, pg/m^3	GOM, pg/m^3	Source
Guiyang, China	Urban	Nov 2001 – Nov 2002	Tekran 2537	8.40 ± 4.87			Feng et al., 2004
		Aug–Dec 2009	Tekran 2537-1130-1135	9.7 ± 10.2	368 ± 676	35.7 ± 43.9	Fu et al., 2011
Chongqing, China	Urban	Aug 2006 – Sep 2007	Lumex RA-915+	6.74 ± 0.37			Yang et al., 2009
Shanghai, China	Urban	Aug–Sep 2009	Tekran 2537	2.7 ± 1.7			Friedli et al., 2011
Ningbo, China	Urban	Oct 2007 and Jan 2008	Lumex RA-915+	3.79 ± 1.29			Nguyen et al., 2011
Seoul, South Korea	Urban	Feb 2005 – Feb 2006	TGM: Tekran 2537 PBM and GOM: Manual	3.22 ± 2.10	23.9 ± 19	27.2 ± 19.3	Kim et al., 2009
Tokai-mura, Japan	Urban	Oct 2005 – Aug 2006	Mercury/AM-3, Nihon	3.78 ± 1.62			Osawa et al., 2007
Cape Hedo, Japan	Remote	Oct 2007 to present	Tekran 2537	1.9 ± 0.5	2.2 ± 4.2	1.3 ± 3.1	Japan Ministry of Environment, 2012
Jeju Island, Korea	Remote	May 2006 – May 2007	Manual method	3.85 ± 1.68			Nguyen et al., 2010
An-Ayun Island, Korea	Remote	Dec 2004 – Apr 2006	Mercury/Am-2, Nippon	4.61 ± 2.21			Nguyen et al., 2007
Cape Hedo, Japan	Remote	March – May 2004	Tekran 2537-1130-1135	2.04 ± 0.38	4.5 ± 5.4	3.0 ± 2.5	Chand et al., 2008
Mt. Gongga, China	Rural-affected	May 2005 – July 2007	TGM: Tekran 2537 PBM and GOM: Manual	3.98 ± 1.62	30.7 ± 32.1	6.2 ± 3.9	Fu et al., 2008a,b
Mt. Changbai, China	Rural-affected	Aug 2005 – Jul 2006	Tekran 2537-1130-1135	3.58 ± 1.78	77 ± 136	65 ± 84	Wan et al., 2009a,b
Chengshantou, China	Rural-affected	Jul 2007 – May 2009	Lumex RA-915+	2.31 ± 0.74			Ci et al., 2011
Mt. Changbai, China	Remote	Oct 2008 – Oct 2010	Tekran 2537	1.60 ± 0.51			Fu et al., 2012a
Mt. Leigong, China	Remote	May 2008 – May 2009	Tekran 2537	2.80 ± 1.51			Fu et al., 2010a
Mt. Waliguan, China	Remote	Sep 2007 – Aug 2008	TGM: Tekran 2537 PBM and GOM: Manual	1.98 ± 0.98	19.4 ± 18.1	7.4 ± 4.8	Fu et al., 2012b
Shangri-La, China	Remote	Nov 2009 – Nov 2010	TGM: Tekran 2537 PBM and GOM: Manual	2.59 ± 1.33	43.5 ± 41.6	8.2 ± 9.4	Zhang et al., 2012a
Lulin, Taiwan, China	Remote	Apr 2006 – Dec 2007	Tekran 2537-1130-1135	1.73 ± 0.61	2.3 ± 3.9	12.1 ± 20.0	Sheu et al., 2010

Speciated atmospheric Hg measurements have been conducted in Taiwan, China. The Lulin Atmospheric Background Observatory is on the summit of Mt. Front Lulin in central Taiwan (Sheu et al., 2010). Variation in GEM concentrations at Lulin station was partially determined by the Asian Monsoon. During autumn, winter, and spring, increased outflows of atmospheric Hg from mainland China arrived at Lulin station.

3.4.1.4 Polar regions (Arctic and Antarctica)

The discovery of AMDEs at Alert (Canadian Arctic) in 1995 (Steffen et al., 2008) revolutionised the understanding of Hg cycling in polar regions while stimulating research into atmospheric Hg processes and their impact on this fragile ecosystem. The first annual time series of atmospheric Hg concentrations in the Arctic was obtained at Alert in 1995 (Schroeder et al., 1998). GEM depletion from the Arctic boundary layer has been observed at several locations throughout the Arctic (Sprovieri et al., 2005; Steffen et al., 2008) highlighting that AMDEs occur from the snow surface (Berg et al., 2003; Sprovieri et al., 2005; Sommar et al., 2007; Steffen et al., 2008) up to a maximum altitude of 1 km (Banic et al., 2003). Simultaneous depletion of boundary layer Hg and O_3 have been observed to occur annually at numerous maritime circumpolar sites (Schroeder et al., 1998; Ebinghaus et al., 2002; Lindberg et al., 2002; Skov et al., 2004). The reason for the rapid decrease in both Hg and O_3 concentrations is believed to be reaction with halogen, and in particular Br-containing compounds. Figure 3.10 shows the production of atmospheric Br closely connected to refreezing leads where bromide is pushed out to the surfaces during the refreeze of seawater under sunlight conditions and the possible fate of Hg after its chemical reactions with Br compounds and it is deposited.

During GEM depletion events dramatically increased levels of both gaseous oxidised mercury (GOM; formerly named reactive gaseous mercury, RGM) and/or $PBM_{2.5}$ are observed (Lu et al., 2001; Lindberg et al., 2002; Lu and Schroeder, 2004; Sprovieri et al., 2005; Steffen et al., 2008). Lindberg et al. (2002) reported the first and highest measured concentration levels of GOM (up to 900 pg/m^3) during AMDEs at Barrow (Alaska) and showed a strong correlation between GOM production and UV-B radiation and with increased surface snow Hg concentrations. Calculations of multi-year trends in GOM and $PBM_{2.5}$ at Alert were also performed (Cole et al., 2012), indicating increases from 2002 to 2009 in both GOM and $PBM_{2.5}$ during spring when concentrations are highest.

As previously mentioned (Section 3.4.1.2), ten-year records of TGM were recently analysed from Canadian mid-latitude, sub-Arctic, and High Arctic sites (Cole et al., 2012). The High

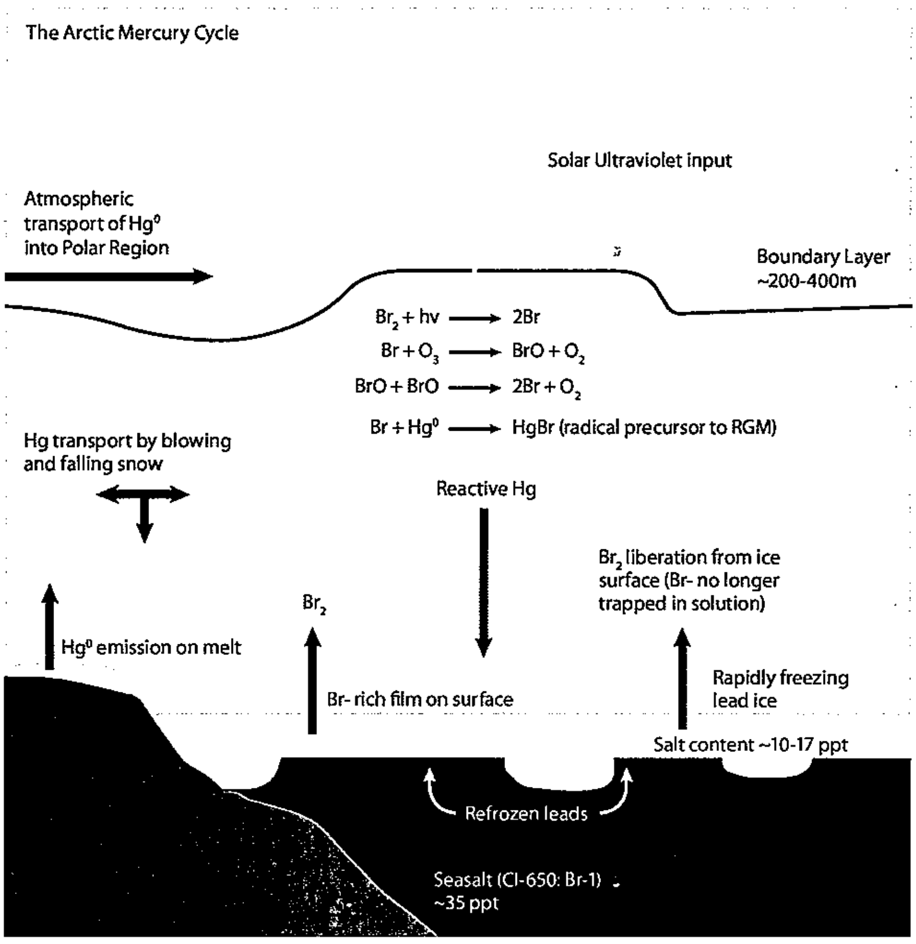


Figure 3.10 Schematic description of atmospheric bromine production and the possible fate of mercury after its chemical reactions with bromine-containing compounds and its deposition. Source: AMAP/UNEP (2008).

Arctic sites examined in that study were Alert (Nunavut, Canada) and Zeppelin station (Svalbard, Norway). At these sites, a different temporal pattern was observed than for the mid-latitude and sub-Arctic sites, given that in the High Arctic, Hg behaves differently with much more variability during the seasons (i.e., springtime chemistry). In particular, no trend has been observed at Zeppelin station whereas in the Canadian High Arctic (Alert) a slight GEM decreasing trend was observed (-0.6% per year). In comparison to the mid-latitudes, this highlights the idea that Hg chemistry is different in the Arctic compared to other parts of the world, both during AMDEs and in terms of long-term behaviour. This may be due to the overlap of several mechanisms, including long-range transport from lower latitudes, and chemical interactions with the sea ice and/or snow pack through surface Br reactions (Simpson et al., 2007; Cole et al., 2012).

Springtime AMDEs have also been observed in Antarctica. During Antarctic spring 2000, Hg ground-level concentrations were measured by Ebinghaus et al. (2002) at Neumayer (70°39'S, 8°15'W), the coastal German Research Station. During the same period enhanced column densities of BrO (GOME satellite data) were observed over the sea ice around the Antarctic continent (Ebinghaus et al., 2002), and enhanced boundary layer BrO concentrations were observed using differential optical absorption spectroscopy (DOAS) (Friess et al., 2001; Dommergue et al., 2010).

3.4.2 Mercury wet deposition measurements and trends

3.4.2.1 Europe

Wängberg et al. (2007) summarised measurements of Hg wet deposition at six EMEP sites along the North Sea coast from 1995 to 2002. On average, a decreasing trend was observed from the first half (1995–1998) to the second half (1999–2002) of the study. On average, the total Hg wet deposition at two sites (Råö and Rörvik) declined substantially over three-year increments from 1987 to 2002, perhaps due to reductions in regional Hg emissions; however changes in meteorological patterns over time could not be assessed or excluded as a factor controlling Hg wet deposition. A slight north-south gradient of increasing concentrations of Hg in precipitation was also reported and may reflect the positions of emission sources in central Europe.

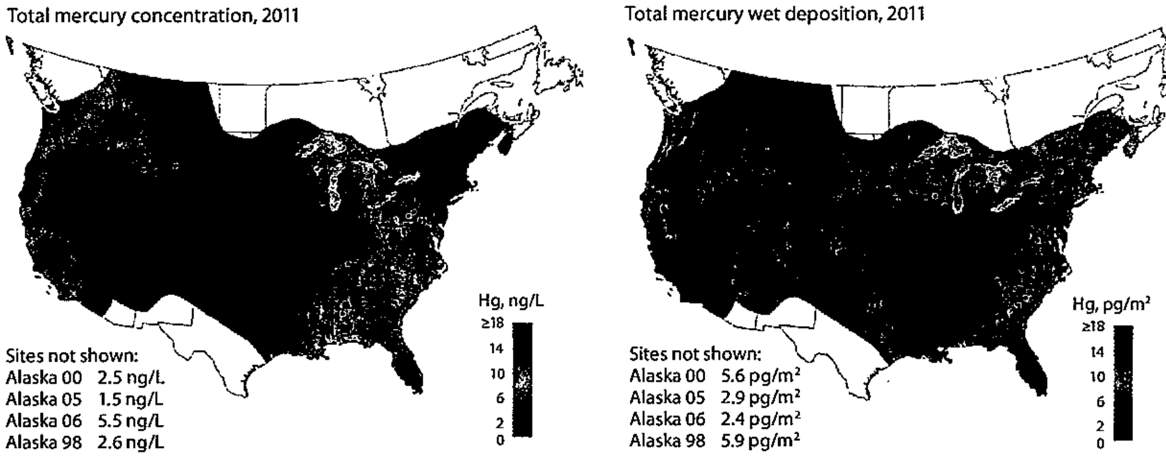
Several atmospheric Hg monitoring sites in Europe, including sites within EMEP, were recently incorporated into the GMOS project. In the future it will be possible to utilise these precipitation measurements to further understand both the spatial and temporal distribution of Hg in wet deposition.

3.4.2.2 North America

The continued development of Hg monitoring programmes over the past 20 years in the United States and Canada has provided an opportunity to explore long-term trends in Hg wet deposition. Keeler and Dvonch (2005) presented ten years (1994–2003) of atmospheric Hg observations in the Great Lakes region, where daily-event precipitation samples were collected for Hg and trace elements (Landis and Keeler, 1997). Results from three sites in Michigan (Eagle Harbor, Pellston, Dexter) demonstrated a strong decreasing north-south gradient in the amount of Hg wet deposition. An obvious trend in annual Hg wet deposition over time was not observed, suggesting that despite efforts to control Hg emissions, emission sources in the southern Great Lakes region continually impacted the levels of Hg wet deposition. Similar measurements of event-based Hg wet deposition in the Chicago (Landis et al., 2002; Landis and Keeler, 2002) and Detroit urban areas, as well as the highly industrialised Ohio River Valley (Keeler et al., 2006; White et al., 2009) have further demonstrated the significant contribution from local and regional anthropogenic sources to the observed levels of Hg in wet deposition in the Great Lakes basin. Specifically, 70% of Hg wet deposition in Steubenville (Ohio) was attributed to emissions from coal combustion, based on the application of multivariate statistical receptor models to event-based wet-only measurements of Hg and trace element wet deposition (Keeler et al., 2006). More recently, similar analyses applied to four event-based wet-only monitoring sites in the state of Illinois, also located in the industrialised U.S. Midwest, suggested that coal combustion emissions were responsible for 50–74% of Hg wet deposition at each site (Gratz et al., 2013b).

Prestbo and Gay (2009) recently summarised ten years (1996–2005) of weekly Hg wet deposition measurements from NADP-MDN sites in the United States and Canada. Results indicated regional differences in precipitation, concentration, and deposition over time. Total Hg deposition was highest in the south-eastern United States, and in all regions Hg wet deposition was greatest during the summer. Several sites in the north-eastern United States and along the east coast displayed decreasing trends in concentration (1–2% per year). This trend was not observed in the U.S. Midwest or in much of the southeast. Most Midwest sites displayed no significant trend in concentration or deposition, while several sites in the southeast displayed significant increases in wet deposition. Four sites in the region between the Midwest and northeast United States displayed patterns of decreasing concentration, increasing precipitation amount, and consequently no significant trend in deposition. These varying trends could be attributed to regional differences in meteorology and source emission impacts. Figure 3.11 presents the most recently available total Hg concentration and wet deposition annual gradient maps from the MDN programme for 2011.

Daily-event precipitation samples collected in Underhill (Vermont) from 1995–2006 were analysed for total Hg and trace element concentrations (Gratz et al., 2009; Gratz and Keeler 2011). Measurements from this site comprise one of the longest



Total mercury concentration, 2011

Sites not shown:
Alaska 00 2.5 ng/L
Alaska 05 1.5 ng/L
Alaska 06 5.5 ng/L
Alaska 98 2.6 ng/L

Total mercury wet deposition, 2011

Sites not shown:
Alaska 00 5.6 pg/m²
Alaska 05 2.9 pg/m²
Alaska 06 2.4 pg/m²
Alaska 98 5.9 pg/m²

Figure 3.11 Total mercury concentration and wet deposition annual gradient maps for North America from the NADP-MDN programme for 2011. Source: http://nadp.sws.uiuc.edu/mdn/annualmdnmaps.aspx.

available Hg wet deposition datasets in the world. A statistically significant trend in annual Hg wet deposition over time was not detected, despite emissions reductions in the United States in the late 1990s with the implementation of stack controls on municipal and medical waste incinerators. In contrast, annual volume-weighted mean (VWM) Hg concentration declined in conjunction with an increase in the total annual precipitation amount. The declines in concentration appeared to be related to local-scale meteorological and climatological variability rather than to a reduction in emissions of Hg to the atmosphere (Gratz et al., 2009). Multivariate and hybrid receptor modelling analyses further revealed that, of the nearly 80% of measured deposition accounted for by the Positive Matrix Factorisation (PMF) multivariate statistical receptor model, coal combustion consistently contributed to approximately 60% of Hg wet deposition. Using back-trajectory cluster analysis and hybrid receptor modelling techniques, the majority of Hg deposition at Underhill was linked to transport from the U.S. Midwest and east coast where the density of coal-fired utility boilers in the United States is greatest (Gratz et al., 2009; Gratz and Keeler 2011).

Risch et al. (2012) recently reported on Hg wet deposition at 37 sites in the North American Great Lakes region from 2002 to 2008. A decreasing trend in Hg concentration was observed at eight sites, and increasing trends in concentration were observed at six sites. Much of the region saw an increase in annual precipitation amount during this period. Over the course of the study, Hg wet deposition was largely unchanged in the Great Lakes region and surrounding areas, and any significant trends in deposition did not correspond with trends in concentration. Overall, it was suggested that any observed declines in concentration were offset by increases in precipitation amount, and as such the total wet deposition amount remained largely unchanged.

These studies revealed regional differences in Hg concentration, precipitation, and Hg deposition patterns in the United States and Canada, and over time a large-scale decline in Hg deposition has not been observed. This overall observation that Hg wet deposition has not declined over time at many North American locations appears to be somewhat in contrast to the recently reported declines in background GEM concentrations at several remote sites around the world, suggesting that there are still many questions remaining about atmospheric Hg processes, including chemistry, transport, and deposition, at different locations and on different temporal or spatial scales.

Continued long-term monitoring in North America will demonstrate whether new legislation, such as the recently issued Mercury and Air Toxics Standards that regulate Hg emissions from utility boilers and other sources, have a significant impact on the amount of Hg deposited to the environment. In addition, in light of current observations and projected patterns of global climate change, it is plausible that changes in the distribution and intensity of precipitation events may occur. Given that Hg wet deposition amounts vary with geographical location, proximity to emission sources, speciation of emissions, and meteorological conditions prior to and during storm events, it is possible that the spatial distribution in Hg wet deposition will also change with future variability in precipitation patterns and storm intensity. The continued operation of regional and global monitoring networks will allow for investigating these deposition patterns in future climate scenarios.

3.4.2.3 Asia

A summary of total Hg concentrations in precipitation and wet deposition Hg fluxes in Asia is presented in Table 3.6. Total Hg concentrations in precipitation obtained from urban and remote areas of Asia were in the ranges 7.8–30.7 ng/L and 4.0–36.0 ng/L, respectively. Total Hg wet deposition fluxes in urban and remote areas of Asia were in the ranges 13.1–20.2 $\mu g/m^2/y$ and 5.8–26.1 $\mu g/m^2/y$, respectively. Total Hg concentrations in precipitation and wet deposition fluxes in Asia are higher than those observed in urban areas of North America (Landis and Keeler, 1997; Guentzel et al., 2001; Keeler et al., 2006). Total Hg concentrations in urban areas

Table 3.6 Summary of total mercury concentrations in precipitation and atmospheric total Hg deposition fluxes in Asia.

Location	Period	Classification	Precipitation, ng/L	Flux, µg/m^{2}/y	Source
Chongqing, China	Jul 2010 – Jun 2011	Urban	30.7		Wang et al., 2012a
Guiyang, China	Jul–Sep 2008	Urban	18.0		Liu et al., 2011
Wujiang, China	Jan–Dec 2006	Rural-affected	36.0	34.7	Guo et al., 2008
Mt.Leigong, China	May 2008 – May 2009	Remote	4.0	6.1	Fu et al., 2010a
Mt.Gongga[a], China	Jan–Dec 2006	Remote	9.9	9.1	Fu et al., 2008b
Mt.Gongga[b], China	May 2005 – Apr 2007	Remote	14.3	26.1	Fu et al., 2010b
Mt.Changbai, China	Aug 2005 – Jul 2006	Remote	13.4	8.4	Wan et al., 2009b
Japan	Dec 2002 – Nov 2003	Urban	7.8–9.4	13.1–16.7	Sakata and Marumoto, 2005
Japan	Dec 2002 – Nov 2003	Remote	5.0–9.6	5.8–17.7	Sakata and Marumoto, 2005
Seoul, South Korea	Jan 2006 – Dec 2007	Urban	10.1–16.3	16.8–20.2	Seo et al., 2012
Chuncheon, South Korea	Aug 2006 – Jul 2008	Remote	8.8	9.4	Ahn et al., 2011

[a] Elevation of the sampling site was 1600 m a.s.l.; [b]elevation of the sampling site was 3000 m a.s.l.

of China were much higher than those in Japan and South Korea (Table 3.6). This was mostly attributed to the elevated $PBM_{2.5}$ and GOM concentrations in urban areas, which may be readily scavenged by precipitation.

With the exception of the study in Wujiang, China, total Hg concentrations in precipitation and wet deposition fluxes in remote areas of Asia were comparable to those obtained from the U.S. and Canadian NADP monitoring sites (Prestbo and Gay, 2009). The mean total Hg concentrations and wet deposition fluxes in Wujiang were much higher than other studies in remote areas of Asia (Guo et al., 2008); however, this may be due to the collection of monthly-integrated bulk precipitation samples in those studies, and given the generally elevated levels of ambient $PBM_{2.5}$ and GOM concentrations in China it is likely that dry deposition of $PBM_{2.5}$ and GOM substantially contributed to the total Hg in bulk precipitation samples.

3.4.3 Recent advances in measurement and analytical techniques

In addition to the use of the relatively standard measurement techniques for ambient air Hg and Hg wet deposition across these monitoring networks, a number of new measurement and analytical techniques have also been developed in recent years, which will increase understanding of Hg deposition and environmental cycling patterns. For example, in addition to wet deposition it is known that dry deposition can represent an important fraction of the total deposition of Hg to terrestrial and aquatic ecosystems. But unlike precipitation, dry deposition can be more difficult to measure and at this point in time there is no widely accepted measurement technique. Furthermore, to more fully understand atmospheric Hg chemistry and cycling it is necessary not only to quantify total Hg dry deposition but also the speciation of Hg in dry deposition. Measurements of dry deposition have been conducted over both natural and surrogate surfaces to try to understand this process. Examples of currently reported methods for directly measuring Hg dry deposition include surrogate water surfaces (Marsik et al., 2007; Hall et al., 2011), leaf washes (Lyman et al., 2007), and cation-exchange membranes (Lyman et al., 2007). Dry deposition of Hg species has also been indirectly quantified using modelling approaches (Lyman et al., 2007; Marsik et al., 2007; Zhang et al., 2012a). Studies to date suggest that the relative contributions from wet and dry deposition to the total Hg deposition can vary greatly by location depending on local emission sources and atmospheric Hg speciation (Lyman et al., 2007). Further developments in existing measurement techniques, as well as model-measurement comparison, is needed in order to better understand temporal and spatial patterns in Hg dry deposition.

Additionally, there have been efforts recently to develop passive samplers for measuring atmospheric Hg. Availability of such techniques could make it possible to measure atmospheric Hg with reduced power and financial constraints. Examples of more recently reported techniques are mercury vapour adsorption tubes (Brown et al., 2012), and a passive sampler for TGM containing either gold plates or silver wires in an expanded PTFE housing (Gustin et al., 2011). Further method developments of this type are anticipated in the future so that passive sampling methods could be applied on a broader scale.

There is also growing interest in developing new analytical techniques for quantifying Hg in environmental samples. For example, measurements of Hg stable isotope geochemistry have been developed in recent years as a tool for studying Hg biogeochemical cycling (Bergquist and Blum, 2009). Mercury has seven stable isotopes, active redox chemistry, an ability to form covalent bonds, and it commonly transforms between the solid, aqueous, and gas phases. These characteristics allow for significant variations in Hg isotopic composition to be observed across natural samples. Mercury has been observed to undergo both mass-dependent and mass-independent fractionation in a variety of environmental samples, and variations in these signatures may offer insight into Hg biogeochemistry (Bergquist and Blum, 2009, and references therein). Although this is a relatively new area of study, it is one that is growing rapidly. Results published to date suggest that further investigation of this technique will continue to provide insight into atmospheric Hg sources and chemistry (Bergquist and Blum, 2007, 2009; Gratz et al., 2010; Sonke, 2011; Sherman et al., 2012).

3.5 High altitude mercury measurements

3.5.1 High altitude ground-based monitoring stations

In recent years, high-altitude measurements of atmospheric Hg have been reported for the Mt. Bachelor Observatory, Oregon (2700 m a.s.l.) (Jaffe et al., 2005; Swartzendruber et al., 2006; Weiss-Penzias et al., 2006, 2007; Finley et al., 2009), the Storm Peak Observatory, Colorado (3220 m a.s.l.) (Obrist et al., 2008; Faïn et al., 2009) and sites in Nevada, USA (Weiss-Penzias et al., 2009), as well as the Lulin Atmospheric Background Station in Taiwan (2862 m a.s.l.) (Sheu et al., 2010). Weiss-Penzias and colleagues are preparing a comparison of observations from these high elevation sites to identify similar patterns in the observations. Furthermore they have also compared observations with results from the GEOS-CHEM global Hg model. Results suggest that all of these high elevation sites show a common negative relationship between GEM and GOM. The strength of this relationship in the observations varies depending on the site, whereas the model shows a strong relationship at all sites. This systematic difference can be used to understand the behaviour and oxidation of Hg at high elevations. Furthermore, a new analysis from the Mt. Bachelor Observatory suggests that there are additional mechanisms to generate GOM in the free troposphere, which include oxidation within anthropogenic pollution plumes and escape from the marine boundary layer (Timonen et al., 2012).

Speciated atmospheric Hg has also been measured at the Mauna Loa Observatory in Hawaii, where continuous measurements of several important species have been collected since the 1950s. Mauna Loa is a high altitude monitoring station (3397 m a.s.l.) managed by the U.S. National Oceanic and Atmospheric Administration (NOAA). Measurements of speciated atmospheric Hg began in 2001 and are managed by the U.S. Environmental Protection Agency (EPA). Together with speciated Hg, this monitoring effort has also included continuous measurements of ozone, sulphur dioxide, elemental carbon, and other important atmospheric constituents. Mauna Loa, Mt. Bachelor, Storm Peak, the Lulin Atmospheric Background Station, and other previously mentioned high-altitude stations in Asia are also being included in the GMOS ground-based monitoring network, which will allow an in-depth investigation into Hg transport on the global scale through the integration of these high-quality, long-term monitoring datasets.

Within GMOS, several new high-altitude monitoring stations for atmospheric Hg have also been established. In November 2011, the Institute of Atmospheric Pollution Research of the National Research Council of Italy (CNR-IIA) installed a Tekran 2537A Mercury Vapour Analyser at the Ev-K2-CNR Pyramid International Laboratory in the eastern Himalaya Mountains of Nepal. The Pyramid Laboratory (27.95°N, 86.82°E; 5050 m a.s.l.) is a high altitude Italian scientific research centre in Nepal's Khumbu Valley near the Mt. Everest base camp. In April 2012, the Tekran analyser was relocated to the nearby, newly renovated Nepal Climate Observatory at the Pyramid (NCO-P), approximately 200 m from the Pyramid at 5079 m a.s.l. Currently this is the highest altitude monitoring station for atmospheric Hg in the world. Preliminary analyses of TGM measurements from November 2011 to April 2012 suggest that the mean TGM concentration was 1.2 ng/m^3 (range 0.7–2.6 ng/m^3) (Gratz et al., 2012). The data from this location will provide valuable information on the levels of atmospheric TGM in the free troposphere, and in a region of the world where atmospheric Hg measurements are limited but meteorological influences on air quality have previously been observed (Bonasoni et al., 2010).

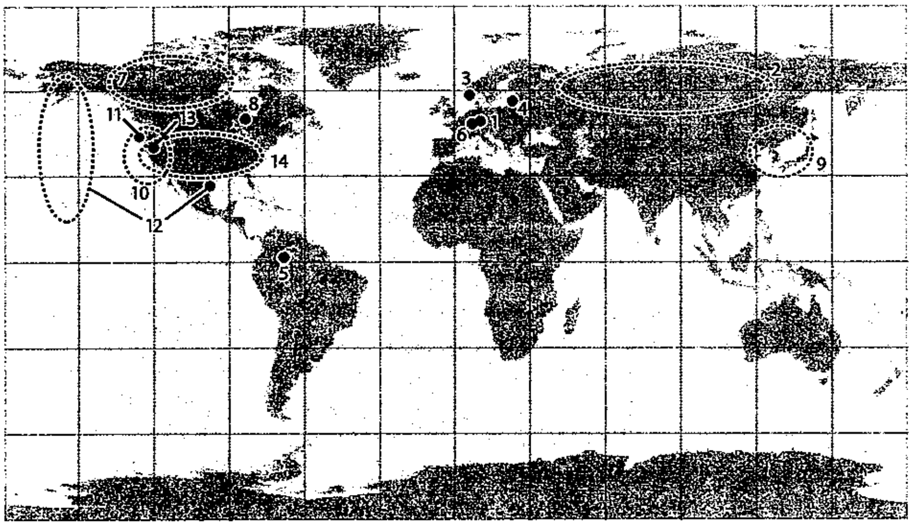
Another interesting addition to the GMOS network has been the French-Italian base, Dome Concordia Station (Dome-C) in Antarctica. Measurements of GEM using the Tekran 2537 Mercury Vapour Analyser began at Dome C (75°06'S, 123°20'E, 3320 m a.s.l.) in December 2011. Dome C is located on the Antarctic plateau, 1100 km from the east Antarctic coast. Monitoring of GEM at Dome-C has already shown some unique results and a surprising level of reactivity (Dommergue et al., 2012). The observed behaviour and trends will be examined more closely as the dataset at this unique site continues to develop. The addition of sites such as Dome C and Ev-K2-CNR to the GMOS network will contribute greatly to the investigation and understanding of atmospheric Hg on the global scale.

3.5.2 Aircraft measurements

3.5.2.1 Campaign-based aircraft measurements

Because Hg is globally distributed through the atmosphere, aircraft observations are a key component for understanding

Figure 3.12 Approximate locations of all known aircraft-based airborne Hg measurements around the world to 2011 (except CARIBIC). Source: Ebinghaus et al. 2012 (and references therein).



1 Slemr et al., 1985
2 Kvietkus et al., 1985, 1995
3 Brosset, 1987
4 Kvietkus et al., 1995
5 Artaxo et al., 2000
6 Ebinghaus and Slemr, 2000
7 Banic et al., 2003
8 Friedli et al., 2003
9 Friedli et al., 2004
10 Radke et al., 2007
11 Swartzendruber et al., 2008
12 Talbot et al., 2008
13 Swartzendruber et al., 2009
14 http://www.atmos.washington.edu/jaffegroup/modules/NAAMEX/

the vertical distribution. Given that airborne Hg measurements are highly demanding and challenging, relatively few airborne Hg measurements have been carried out. The introduction of the automated Tekran instrument enabled the first highly resolved aircraft measurements of the spatial distribution of Hg in the atmosphere (Ebinghaus and Slemr, 2000; Banic et al., 2003; Friedli et al., 2003). Figure 3.12 shows the approximate location of all known airborne Hg measurements around the world, which were obtained on 14 individual measurement aircraft campaigns and published between 1976 and 2009. Many of these measurements were made as individual campaigns with specific objectives and are thus limited in region and time.

Most aircraft measurements have considered only GEM or TGM (Banic et al., 2003; Ebinghaus et al., 2007; Talbot et al., 2008; Slemr et al., 2009; Swartzendruber et al., 2009 and references therein). A summary of the vertical Hg profiles published in the peer-reviewed literature are summarised in Figure 3.13 (Swartzendruber et al., 2009). The vertical gaseous Hg distribution (TGM and GEM) is more or less constant with concentrations ranging from 0.5 to 2.0 ng/m^3.

Very recently, new instrumentation has been developed to measure oxidised Hg compounds as well (Lyman and Jaffe, 2012). Measurements of total Hg, GOM, and O_3 were collected during a flight across the Great Lakes region of the US, in which the aircraft encountered a tropospheric fold with high concentrations of GOM. The results demonstrate that aircraft can be used to measure the complete suite of Hg species in the atmosphere.

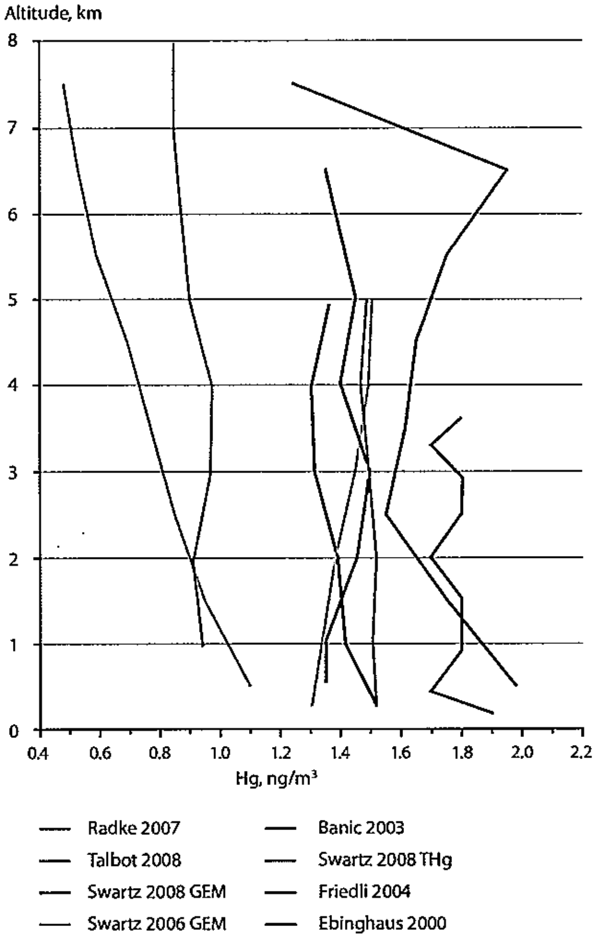


Figure 3.13 Comparison of known vertical gaseous mercury profiles (TGM and GEM). Source: Swartzendruber et al., 2009 (and references therein).

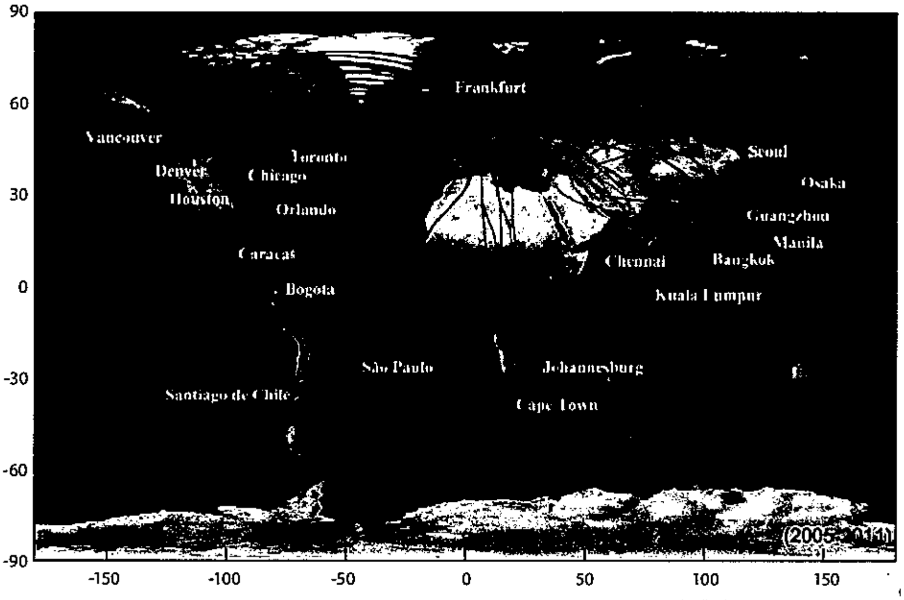
3.5.2.2 The European CARIBIC project

CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) is a scientific project designed to study and monitor important chemical and physical processes in the Earth's atmosphere over the long-term. Detailed and extensive measurements of atmospheric gases and trace compounds are made during long distance flights by a commercial passenger aircraft (Airbus A340-600; 'Leverkusen'). CARIBIC deploys an airfreight container with automated scientific apparatus connected to an air and particle (aerosol) inlet under the aircraft (Brenninkmeijer et al., 2007). In addition to these campaign-based aircraft measurements, monthly intercontinental CARIBIC flights since May 2005 have generated detailed measurements of the large-scale distribution of atmospheric Hg (Ebinghaus et al., 2007; Slemr et al., 2009). The typical monthly measurement sequence includes four intercontinental flights with a total flight time of about 40 hours (Figure 3.14).

The container holds automated analysers for TGM, CO, O_3, NO, NO_y, CO_2, total and gaseous water vapor, oxygenated organic compounds, fine particles (three counters for particles with diameters > 4 nm, > 12 nm, and > 18 nm), an optical particle counter for particles > 150 nm, and instruments for continuous measurements of water isotopologues and methane (CH_4). Up to 116 whole air samples and 16 aerosol samples are also collected. Air samples are later analysed for greenhouse gases (Schuck et al., 2009), hydrocarbons (Baker et al., 2010), and halocarbons (Oram et al., 2012), while aerosol samples are analysed for their morphology and elemental composition (Nguyen et al., 2008). Mercury is measured by a Tekran 2537 analyser. The inlet tubing is PFA-lined and consists of high-volume circular tubing with a temperature regulated manifold (40 °C) and a short PFA connection to the instrument at the internal container temperature (about 30 °C). For operation at cruise altitudes around 10 km the air sample is compressed from ambient pressure to about 500 hPa (needed to operate the Tekran instrument with its internal pump). At present the Tekran is operated using a 10 minute sampling interval to obtain a detection limit and precision of ~0.05 ng/m³. Reported results are corrected (Slemr et al., 2009) at standard temperature and pressure.

Since May 2005, almost 300 intercontinental flights have provided Hg measurements in the upper troposphere and lower stratosphere (Slemr et al., 2012). TGM concentrations are always lower in the lower stratosphere than the upper troposphere. In both locations, TGM behaves in a similar manner to other trace species with ground sources and stratospheric sinks (e.g., CO and CH_4) but, unlike these other species, Hg can only be transformed into other Hg species (i.e., $PBM_{2.5}$) which escape detection by the analytical instrumentation. High $PBM_{2.5}$ concentrations together with high particulate Br concentrations in the lower stratosphere were reported by Murphy et al. (1998, 2006). An attempt to quantify Hg on the aerosol samples collected during the CARIBIC flights was unsuccessful because the semi-volatile Hg compounds on the particles are pumped away during analysis in vacuum by proton-induced X-ray emission, perhaps suggesting that TGM is more likely to be converted to semi-volatile Hg halogenides (e.g., $HgBr_2$, $HgCl_2$) than to much less volatile HgO. An inverse relationship between TGM and particle concentration has also been observed in the deep stratosphere (Slemr et al., 2012).

The transformation rate of TGM to $PBM_{2.5}$ can be calculated using the long-lived tracer SF_6. Correlations of TGM with SF_6 suggest a seasonally dependent TGM conversion rate of about 0.43 ng/m³/y resulting in a stratospheric TGM lifetime of about 2 years. This lifetime is longer than the several weeks



Satellite image: NASA Earth Observatory

Figure 3.14 Intercontinental flight tracks of the CARIBIC project between 2005 and 2011. Source: www.caribic-atmospheric.com.

recently suggested by Lyman and Jaffe (2012) and possibly closer to the lifetime of 1 year estimated by Holmes et al. (2010a) using the GEOS model with Br oxidation chemistry (Slemr et al., 2012).

3.6 Global mercury modelling

3.6.1 Introduction

The transport and deposition of Hg depend to a very great extent on its oxidation state. As previously mentioned, GEM in the atmosphere generally oxidises relatively slowly, it deposits slowly because of its high (for a metal) vapour pressure and due to its low solubility it is inefficiently scavenged by cloud droplets and precipitation. On the other hand, GOM compounds deposit rapidly and are efficiently scavenged due to the higher solubility of GOM. Hence GEM is subject to long-distance transport, whereas GOM is, for the most part, dry or wet deposited close to the point of emission or formation. Mercury also exists in the atmosphere associated with particulate matter, either as a component of the particulate itself or adsorbed onto the particulate, and in equilibrium with the Hg and its compounds present in the gas phase.

When modelling the transport and deposition of Hg it is necessary to have a good understanding of the speciation of Hg emissions. It is equally important that the chemistry of the atmosphere is accurately represented in terms of the potential oxidants of Hg, because as already mentioned it is the oxidation state of Hg which determines how far it is transported and how rapidly it is deposited. However as discussed in Section 3.2 there are still some fundamental uncertainties in understanding of atmospheric Hg chemistry. Modelling studies involving Hg range from process modelling where detailed physico-chemical models are employed to study the mechanisms involved in individual processes, to regional transport and chemistry models where relatively high spatial resolution models are used to investigate regional-scale Hg deposition and concentration variations, to global models used to investigate long-range Hg transport and deposition patterns and their long-term variation. The importance of global models has become more evident recently as assessments of regional modelling studies have highlighted the importance of the choice of boundary conditions for the modelling domain. It is now accepted that regional models require boundary (and initial) conditions supplied by the output from global models. The following parts of Section 3.6 discuss the approaches used in global and regional models to represent the atmospheric processes influencing Hg transport and deposition.

Atmospheric chemical transport models are powerful tools for assessing pollution levels and transport pathways for environmental contaminants, given the limited coverage of existing monitoring networks. Contemporary Hg models complement direct measurements by providing spatial coverage and detailed information on ambient concentrations and deposition levels, estimates of source attribution, an explanation of historical trends and projections of future changes in pollution. The models can also be used in combination with measurement data to investigate the physical and chemical processes controlling the fate of Hg in the atmosphere as well as to evaluate emission inventories.

3.6.2 Global patterns of mercury air concentration and deposition

The global distribution of atmospheric Hg concentrations and deposition were simulated using an ensemble of contemporary models within the HTAP multi-model experiment (Travnikov et al., 2010). The results show (Figure 3.15a) that the highest GEM concentrations (> 2 ng/m³) are characteristic of major industrial regions – East and South Asia, Europe, North America, and South Africa. There is also a pronounced gradient in the surface GEM concentrations between the southern and northern hemispheres owing to the positions of major anthropogenic emission sources.

Deposition of atmospheric Hg is mostly the result of wet scavenging and dry deposition of the oxidised forms (GOM and $PBM_{2.5}$). Depending on the origin of these Hg species, the deposition flux can be divided into two components:

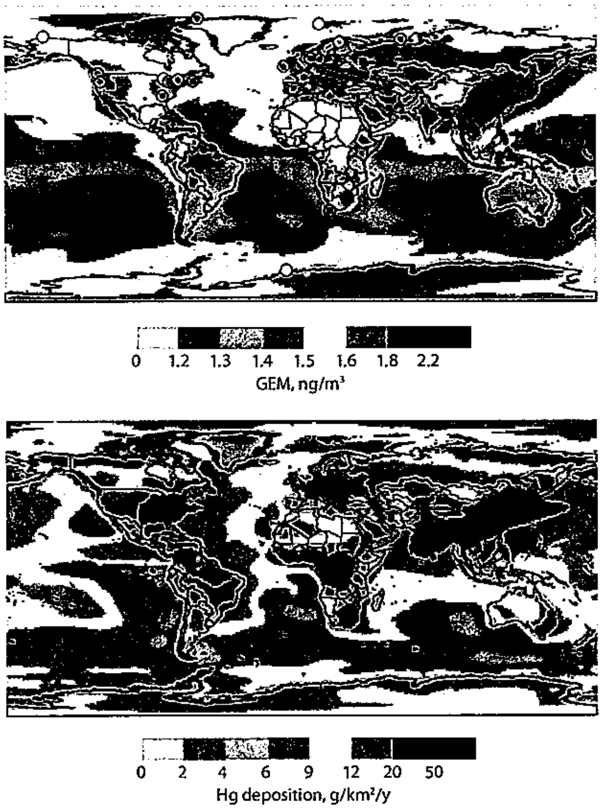


Figure 3.15 Global distribution of ensemble mean annual GEM concentration in ambient air (a) and annual mercury total deposition (b) in 2001. Circles represent long-term observations from the AMAP, EMEP, CAMnet networks and at some other monitoring sites. Source: Travnikov et al. (2010) and references therein.

the first consists primarily of emitted short-lived forms; the second is defined by oxidation of GEM in the atmosphere. The former is prevalent in the vicinity of emission sources, whereas the latter dominates in remote regions. An additional process contributing to Hg deposition is air-surface exchange (mainly associated with vegetated surfaces) of GEM. All these mechanisms are reflected in the simulated global Hg deposition pattern (Figure 3.15b). High Hg deposition fluxes were obtained in major industrial regions and over some remote areas characterised by high precipitation. In general, deposition fluxes are higher in low to mid-latitudes because of higher concentrations of the main oxidants and precipitation amount. Elevated deposition levels are also characteristic of the polar regions due to AMDEs during the spring. The lowest deposition fluxes occur inland in Antarctica and Greenland.

Estimates of annual Hg deposition to various land and water surfaces globally are given in Table 3.7.

The models differ considerably in their estimates of total deposition in particular regions. Smaller differences (below a factor of 2) are characteristic of the industrial regions largely affected by local anthropogenic sources, whereas the largest discrepancies (a factor of 3 or more) are over remote regions and regions with small anthropogenic emissions. The main differences in the model results are explained by the different approaches used in the spatial distribution of natural emissions and re-emissions, the major oxidants of GEM in the atmosphere and the reaction products included in the models (AMAP, 2011).

Table 3.7 Modelled Hg deposition to various world regions and ocean basins in 2005, t/y.

	GRAHM	GEOS-Chem	GLEMOS	CMAQ-Hg[a]	DEHM[a]
Deposition to land					
Sub-continent					
Australia, New Zealand & Oceania	97	155	57	-	-
CIS & other European countries	346	418	220	193	198
Central America and the Caribbean	44	60	27	49	17
EU27	102	104	58	71	63
East and Southeast Asia	490	524	381	420	334
Middle Eastern States	70	89	29	59	31
North Africa	53	54	16	28	13
North America	317	420	208	197	169
South America	274	443	227	-	-
South Asia	132	164	90	-	-
Sub-Saharan Africa	331	516	249	-	-
Total	2256	2947	1562	1018	825
Deposition to oceans					
Ocean basin					
Antarctic	45	35	11	-	-
Arctic	216	304	163	65	133
Atlantic	648	1410	919	1063	318
Baltic	12	14	8	7	7
Black Sea	13	18	11	12	10
Caspian Sea	6	10	7	5	3
Indian	525	1343	689	646	112
Mediteranean	42	49	34	41	29
North Sea	14	18	11	12	11
Pacific	1358	2733	1767	1576	657
Total	2878	5934	3619	3425	1280

[a] Northern hemisphere only.

3.6.3 Estimates of mercury intercontinental transport

The impact of intercontinental atmospheric transport of Hg on regional contamination levels was studied by Travnikov et al. (2010). The four models involved in the study differed significantly in their formulation of atmospheric transport, chemistry, and natural and secondary emissions. In spite of considerable differences in deposition estimates, the participating models were consistent in their source attribution. Typically domestic sources make the largest contribution (15–55%) to Hg deposition in respective regions. The contribution of foreign anthropogenic sources to annual Hg deposition fluxes varies from 10% to 30% on average anywhere on the globe (Figure 3.16). Where domestic sources are low their contribution to deposition can be less than that from foreign sources (Travnikov et al., 2010). Among the major contributors, East Asia is the most dominant source region, with annual contributions from anthropogenic sources of 10–14% to Hg deposition in other regions. Natural and secondary emissions contribute 35–70% of total deposition to most regions.

These results shown in Figure 3.16 are generally consistent with findings from previous model studies. Seigneur et al. (2004) found that North American anthropogenic emissions contributed 25–30% and Asian anthropogenic emissions about 20%, to Hg deposition in the United States. Travnikov and Ilyin (2005) estimated that around 40% of annual Hg deposition to Europe originated from distant sources (Asia 15%, North America 5%). The same study indicated that North America is particularly affected by emission sources on other continents, with up to 67% of total deposition from foreign anthropogenic and natural sources (Asia 24%, Europe 14%). More recent results obtained with a coupled land–ocean–atmosphere model (Selin et al., 2008; Corbitt et al., 2011) distinguished between natural emissions and re-emissions to Hg deposition over the United States. Present-day Hg deposition in the United States includes about 20% from primary anthropogenic emissions in North America, 22% from primary anthropogenic emissions outside North America (mostly East Asia), 26% from recycling via land and oceans, and 32% from natural origins.

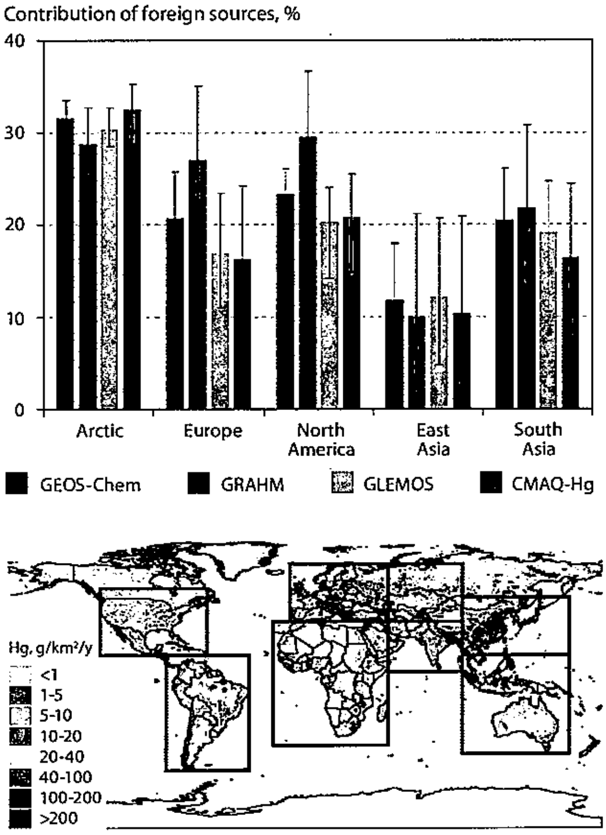


Figure 3.16 (a) Contribution of foreign anthropogenic sources to mercury deposition in different receptor regions in 2005. Bars represent average values and whiskers show the 90%-confidence interval of the parameter variation over a region. (b) Global distribution of anthropogenic mercury emissions in 2005 and location of source regions considered in the analysis – Europe, North America, East Asia, South Asia, Central Asia, Africa, South America, Australia and Oceania. Source: Travnikov et al. (2010).

The above-mentioned models were also employed to investigate Hg pollution in the Arctic (AMAP, 2011). The model ensemble results indicated that the largest anthropogenic contribution to Hg deposition in the Arctic is from East Asia followed by Europe, Central and South Asia, and North America. However, all present-day anthropogenic emissions contribute approximately one-third of total Hg deposition to the Arctic and the other two-thirds are made up by natural sources and re-emissions.

3.6.4 Evaluation of future scenarios

Global Hg models are also used for projecting future emissions scenarios (Travnikov et al., 2010; Corbitt et al., 2011). Possible future changes in Hg pollution levels were simulated by an ensemble of four global and hemispheric models on the basis of three emission scenarios for 2020 (Travnikov et al., 2010). The scenarios represent the status quo conditions (current patterns, practices and uses continue, while economic activity increases in various regions; the 'SQ' scenario); economic progress, and wide implementation of emission control technologies currently used throughout Europe and North America (the 'EXEC' scenario), and implementation of all feasible control technologies to reduce Hg, leading to the maximum degree of emissions reduction (the 'MFTR' scenario) (AMAP/UNEP, 2008). The model ensemble projected consistent changes in levels of Hg deposition in the future. Depending on the emissions scenario applied, Hg deposition is projected to increase by 2–25% (for SQ) or decrease by 25–35% (for EXEC and MFTR) in different industrial regions. In remote regions, such as the Arctic, the changes are expected to be smaller, ranging from an increase of 1.5–5% (SQ) to a decrease of 15–20% (EXEC, MFTR).

Corbitt et al. (2011) applied a global atmospheric model with coupled surface reservoirs to quantify source-receptor relationships on continental scales for the present-day and for 2050 emissions projections (Streets et al., 2009). The projections are based on four emissions scenarios developed by the Intergovernmental Panel on Climate Change (IPCC) (A1B, A2, B1, B2) distinguished by their assumptions regarding industrial growth, energy policy, and emissions control. The worst-case scenario (A1B) assumes heavy use of coal with limited emission control technology, while the best-case scenario (B1) assumes aggressive transition away from fossil fuel energy sources and implementation of efficient control technology. The models results suggest that Hg deposition in 2050 relative to present day is similar in the B1 scenario but increased in the three other scenarios, reflecting the global trend in emissions. In addition, an increasing fraction of HgII in total Hg emissions in the future will result in an increasing relative domestic contribution to deposition (Figure 3.17).

3.6.5 Overview of modelling approaches

Most transport models consider the full chain of Hg processes in the atmosphere: emission from anthropogenic and natural sources/processes, atmospheric transport, chemical transformations, and deposition to terrestrial and oceanic surfaces. The models consider a number of gaseous mercury forms (GEM and GOM) as well as Hg species dissolved in cloud water and Hg bound to particles ($PBM_{2.5}$). Simulated redox chemistry includes Hg reactions with such atmospheric oxidants as O_3, OH, H_2O_2, and/or reactive halogens (Br, BrO, Br_2, Cl, ClO, Cl_2, etc.) (Holmes et al., 2010a; Travnikov et al., 2010; Lin et al., 2012). Most models incorporate oxidation reactions driven by all or some of these substances in their chemical schemes. For instance, oxidation reactions of GEM with O_3 and OH were considered to be the major oxidation mechanisms during the past decade, and allowed reproduction of observed Hg concentrations and wet deposition fluxes on both regional and global scales (e.g., Seigneur et al., 2004; Ryaboshapko et al., 2007a,b; Selin and Jacob, 2008; Travnikov and Ilyn, 2009). However, these chemical mechanisms failed to simulate fast Hg0 oxidation during AMDEs and the diurnal cycle of GOM concentrations in the marine boundary layer (Selin et al., 2007). On the other hand, there has been a successful effort to explain the whole gas-phase Hg oxidation chemistry in the free atmosphere solely in terms of reaction with atomic Br (Holmes et al., 2010a; Amos et al., 2012).

Atmospheric Hg removal processes include scavenging by precipitation (wet deposition) and deposition through interaction with the earth's surface (dry deposition). Wet deposition is commonly distinguished in terms of in-cloud and below-cloud washout and involves oxidised forms of Hg (GOM, $PBM_{2.5}$). GEM does not undergo direct scavenging by precipitation because of its low solubility, but it can be washed out indirectly through dissolution and oxidation in cloud water. Some Hg transport models include explicit treatment of Hg cycling in environmental media other than the atmosphere such as soil, vegetation, snow, sea and freshwater bodies (Selin et al., 2008; Smith-Downey et al., 2010; Soerensen et al., 2010; Durnford et al., 2012).

A number of intercomparison studies have been performed during the last decade to analyse model differences and to quantify uncertainties in the results produced by various models (Ryaboshapko et al., 2007a,b; Bullock et al., 2008, 2009). The most

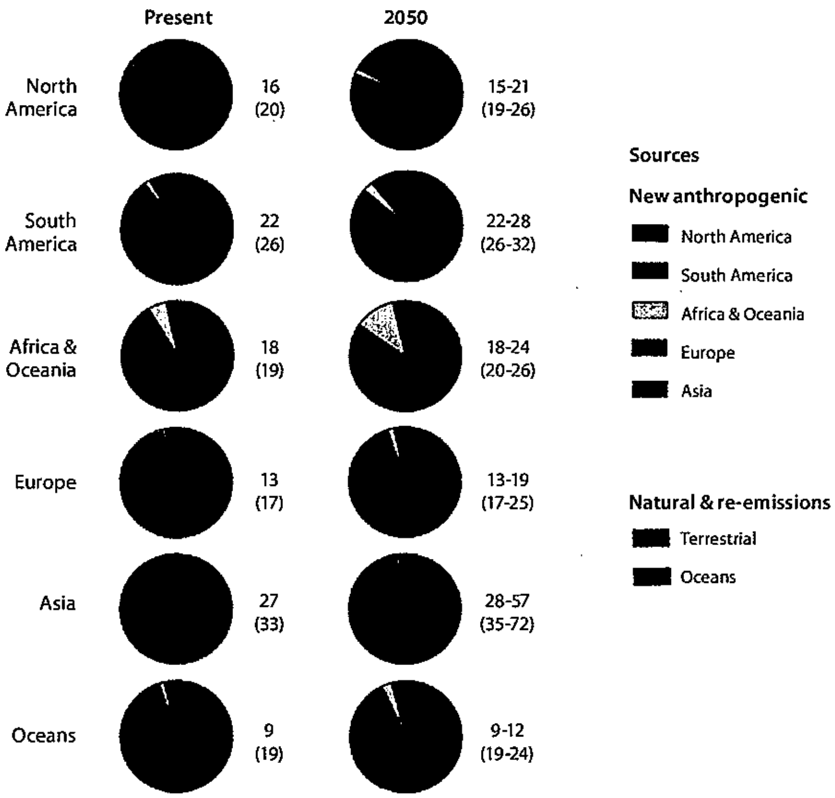


Figure 3.17 Sources of mercury deposited to aggregated world regions for the present-day and for 2050 based on four IPCC emissions scenarios (A1B, A2, B1, B2). Numbers give annual net deposition fluxes to the receptor region (gross deposition fluxes in parentheses) and for 2050 represent the range of the IPCC scenarios. Pie charts show the relative source contributions to deposition. Source: Corbitt et al. (2011).

recent intercomparison was organised within the framework of the Task Force on Hemispheric Transport of Air Pollution (TF HTAP) under the UN Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (LRTAP) and carried out a multi-model evaluation of intercontinental transport of different air pollutants, including Hg, using mainly global and hemispheric models (Pirrone and Keating, 2010; Travnikov et al., 2010). The estimated magnitudes of model uncertainties range from 20%, for the simulated air concentration of GEM, to 80% for the simulated total deposition. However, the model results for the relative source attribution have a smaller uncertainty at about 30%.

3.7 Regional mercury modelling

3.7.1 Introduction

Regional-scale Hg models are necessary to look more closely at areas of particular interest, and the higher spatial resolution employed enables these models to simulate the dispersion and deposition of Hg more accurately than global models.

Local-scale/urban models are employed for investigating Hg concentration and deposition in the immediate vicinity of large emission sources where the influence of regional and global Hg transport is relatively insignificant. These models are Gaussian type or plume models that employ pollutant transport and dispersion from a single emission source and include chemistry and removal processes (Lohman et al., 2006). Regional or continental-scale models address atmospheric dispersion and transport within a continent or a specific region containing numerous emission sources. Most regional Hg models are Eulerian systems that simulate the emission, transport, chemistry and deposition of Hg in three dimension using a fixed grid structure (Cohen et al., 2004; Hedgecock et al., 2006; Pan et al., 2006; Roustan and Bocquet, 2006; Voudouri and Kallos, 2007; Travnikov and Ilyin, 2009). Ambient air Hg concentrations and deposition on regional scales are determined both by regional emissions of Hg and by Hg transported globally. Regional models offer finer horizontal resolution (10–50 km) compared to the generally coarse resolution of global models (100–1000 km) and thus are suitable for detailed examination of Hg distribution within a region. Detailed information on meteorology, chemistry and emissions is often used in these models. Since Hg transports on a global scale, regional Hg models are not self-contained and require initial and lateral boundary conditions of Hg concentration. These concentrations are typically assigned as fixed background values or values extracted from the global Hg model simulations. One problem with this approach is that the regional and global models often use different meteorology, Hg emissions and parameterisations for chemistry and deposition. Use of different global models to define boundary conditions can generate variations in regional patterns of atmospheric Hg concentration, as well as wet and dry deposition (Bullock et al., 2008, 2009; Pongprueksa et al., 2008; Myers et al., 2012). A few nested grid regional models have been developed that make use of a common model to provide simulations at global and regional resolutions using a multi-scale approach (e.g., Zhang et al., 2012b).

3.7.2 Mercury model intercomparison studies

The most comprehensive Hg model intercomparison study to date – NAMMIS (North American Mercury Model Intercomparison Study) – was conducted for North America using three regional models (Bullock et al., 2008, 2009). The study compared the regional Hg models CMAQ-Hg (Community Multi-scale Air Quality model), REMSAD-Hg (Regional Modelling System for Aerosols and Deposition) and TEAM (Trace Element Analysis Model) with each other and with the Hg wet deposition measurements applied in a tightly constrained testing environment, thus allowing a better analysis of the impact of differences in model Hg process parameterisations on the simulations. The three regional models used the same emission inventory data, meteorological fields and initial/boundary conditions as model input. The Hg distributions simulated by three global Hg models, CTM-Hg (Chemical Transport Model for Hg; Shia et al., 1999), GEOS-Chem (Selin et al., 2007) and GRAHM (Global-Regional Atmospheric Heavy Metals Model; Dastoor and Larocque, 2004), were used to specify the initial/boundary conditions for the regional models. MDN Hg wet deposition measurements since the 1990s (Vermette et al., 1995) and from event-based monitoring at the Proctor Maple Research Center near Underhill, Vermont (Keeler et al., 2005) were used to validate the models.

The differences in air concentration of Hg species simulated by the three regional models led to significant differences in the mass balance of Hg fluxes in the domain. Model simulated wet deposition of Hg was strongly influenced by the shared precipitation input, but differences of over 50% were still present. Different formulations of dry deposition parameterisations and Hg speciation resulted in differences of up to a factor of ten in some locations between the models. The study also found that Hg concentration patterns generated by the regional-scale models can be significantly different even when the same initial/boundary condition datasets were used.

Observations show that the greatest Hg deposition flux occurs during summer with the lowest during winter. The models generally reproduce this seasonal pattern regardless of the boundary conditions used. The spring and summer seasons present the most difficulty in simulating wet deposition of Hg perhaps because of largely convective precipitation in North America during these seasons which is harder to predict by the meteorological simulation on which the air-quality models rely to estimate wet deposition. The regional models were able to resolve 45–70% of the observed site-to-site variation in annual Hg wet deposition.

3.7.3 Investigation of Hg contamination in specific regions

Several regional-scale Hg models have been developed and applied for simulations of Hg atmospheric transport and deposition in Europe. An air-seawater coupled regional model (MECAWEx) was used for simulating Hg cycling in the Mediterranean region by Hedgecock et al. (2006). The model output showed that Hg evasion from the sea surface significantly exceeds total (wet and dry) deposition making the Mediterranean Sea a net emitter of Hg. They also found that dry deposition generally exceeds wet deposition in Mediterranean region. A coupled regional/hemispheric Hg modelling system (MSCE-HM) was developed by Travnikov and Ilyin (2009) for operational simulations of transboundary Hg pollution within Europe. They found systematically elevated TGM concentrations (1.6–2 ng/m^3) and wet deposition fluxes (10–20 $\mu g/m^2/y$) in central and southern Europe.

A comprehensive regional Hg model based on the US EPA's Community Multi-scale Air Quality (CMAQ) modelling system for North America was developed by Bullock and Brehme (2002) and recently revised by Baker and Bash (2012). Various versions of CMAQ-Hg have been applied to study Hg processes, distribution, budgets and source attribution in United States (Lin and Tao, 2003; Gbor et al., 2006; Lin et al., 2006, 2007; Sillman et al., 2007). A multi-scale modelling system consisting of a global chemical transport model for Hg (CTM-Hg) and a nested regional model (TEAM) was also applied to estimate Hg deposition over the contiguous United States (Seigneur et al., 2004). Mercury deposition to the Great Lakes was studied in detail with the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Cohen et al., 2004). Zhang et al. (2012b) and Lin et al. (2012) conducted the most recent survey of Hg contamination and source attribution for the United States.

Zhang et al. (2012b) used a high-resolution (0.5° latitude × 0.6° longitude; 40 vertical levels up to 10 hPa) nested grid regional version of the GEOS-Chem global model for North America. The Hg emissions, meteorology, chemistry and deposition are self-consistent between the regional and global domains of the model. They showed that the nested grid model is better at capturing the high spatial and temporal variability of Hg wet deposition over North America compared to the low resolution global version of the model. They also investigated the source attribution of Hg deposition in North America. The results were found to be highly sensitive to the assumed speciation ratio of anthropogenic emissions. With an assumption of a significantly lower ratio of oxidised Hg compared to GEM in the emissions (in-plume reduction), the North American anthropogenic sources contributed to only 10% of the total Hg wet deposition in the United States, compared to 22% in the base simulation. Although there is consistent evidence from several modelling studies that an assumption of in-plume reduction improves the modelling estimates of ambient oxidised Hg concentrations and wet deposition, the reduction mechanism itself is currently unknown (Lohman et al., 2006; Amos et al., 2012; Kos et al., 2012; Zhang et al., 2012b). In contrast, a study by Kolker et al. (2010) measuring speciated Hg in the ambient air at multiple distances downwind from emissions sources found increasing concentration of HgII downwind. See Section 3.2 for a discussion of the assumption regarding in-plume reduction.

Recently, Lin et al. (2012) conducted an extensive source attribution study using CMAQ-Hg for the six sub-regions of the contiguous United States (CONUS) to explore the benefits of the maximum available control technology (MACT) rules proposed by the U.S. EPA. They found that dry deposition accounts for two-thirds of total annual deposition in CONUS, mainly contributed by GOM (about 60% of total deposition). Figure 3.18 shows the relative contribution of different source sectors to Hg deposition in each sub-region on an annual basis. The Hg transport from outside the CONUS region contributes from 68% (Northeast region) to 91% (West Central region) of total deposition. Large point sources are found to contribute up to 75% of deposition near the emission sources. Mercury emissions from the electricity generation sector contributed half the deposition in the Northeast, Southeast, and East Central regions, whereas emissions from natural processes were more important in the Pacific and West Central regions (contributing up to 40% of deposition), suggesting that the implementation of the new EPA MACT standards will significantly benefit only the first three regions.

Pan et al. (2006, 2007, 2008) have previously examined the fate and transport of Hg and its associated uncertainties in the East Asia region using the Hg extension of the Sulfur

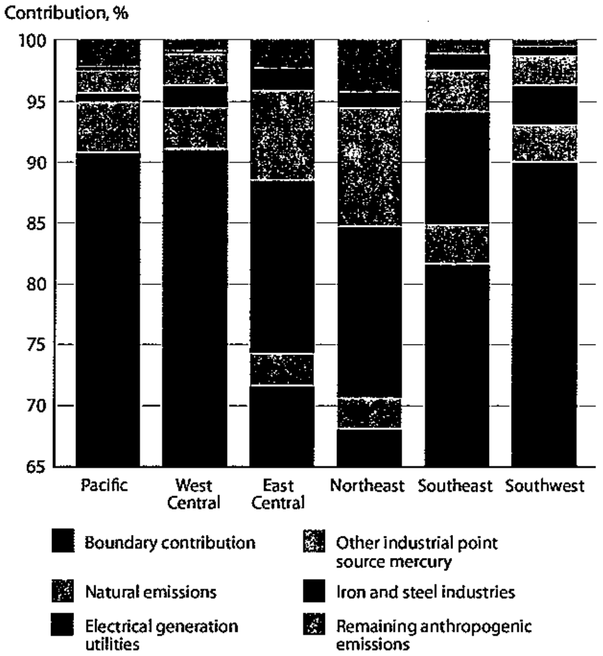


Figure 3.18 Source contribution to annual mercury deposition by the source sectors in six sub-regions of the United States. Source: adapted from Lin et al. (2012).

Transport Eulerian Model (STEM-Hg). More recently, Pan et al. (2010; STEM-Hg) and Lin et al. (2010; CMAQ-Hg), in separate studies, conducted comprehensive assessments of Hg budgets within East Asia and examined outflow from the region. Pan et al. (2010) showed strong seasonal variation in Hg concentration and deposition, with contributions from large point sources. They showed that simulations with different oxidation rates reported for the GEM–O_3 reaction (i.e., by Hall, 1995 vs. by Pal and Ariya, 2004) led to a 9% difference in the modelled mean concentration and a 40% difference in the modelled mean deposition. Pan et al. (2010) estimated annual dry and wet deposition for East Asia in 2001 to be within the range 590–735 t and 482–696 t, respectively, whereas Lin et al. (2010) estimated dry deposition of 425 t and wet deposition of 396 t in 2005. The outflow of Hg caused by East Asian anthropogenic emissions was estimated to be 681–714 t/y by Pan et al. (2010) and in the range 1369–1671 t/y (of which 50–60% was from natural sources) by Lin et al. (2010). Figure 3.19 shows average GEM air concentrations and accumulated dry and wet deposition for July in 2005 over East Asia simulated by CMAQ-Hg. Lin et al. (2010) showed that anthropogenic emissions were responsible for most of the deposition (75%) in East Asia and estimated a net removal of GOM (7–15 t/month) and $PBM_{2.5}$ (13-21 t/month) in the domain, and a net export of GEM (60–130 t/month) from the domain.

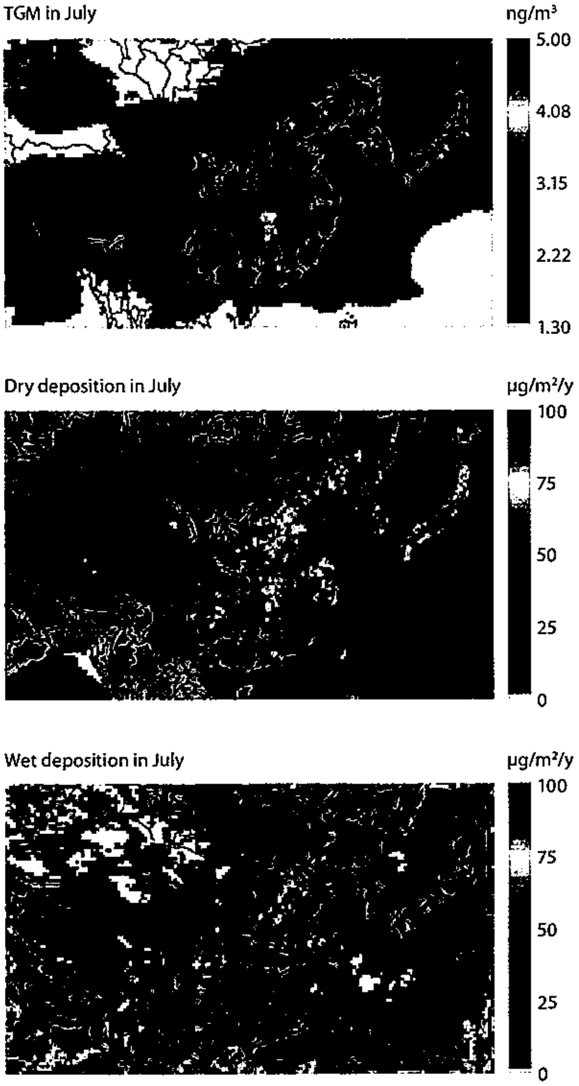


Figure 3.19 Spatial distribution of the monthly average surface air concentrations of total mercury (GEM + GOM+ $PBM_{2.5}$) (a), and monthly cumulative dry deposition (b) and cumulative wet deposition (c) normalised to annual deposition (µg/m²/y). Source: adapted from Lin et al. (2010).

3.7.4 Investigation of the uncertainties in process parameterisations

One of the greatest model uncertainties comes from the chemical mechanism implemented in Hg models. The Hg chemistry parameterisations employed in models are based on limited laboratory studies and there are still questions over which are the key oxidation reactions (Gårdfeldt and Jonsson, 2003; Calvert and Lindberg, 2005). There are uncertainties associated with the kinetic mechanism, the rate constants, and the nature of the products; this is particularly true for the gas phase oxidation of GEM. Understanding the product distribution between the gas and aerosol phases (i.e., GOM vs. $PBM_{2.5}$) is important, because the deposition velocity and removal mechanism vary greatly for the different Hg species.

The CMAQ-Hg regional model has been used to investigate the impact of different gas phase oxidation reaction mechanisms on the simulated monthly wet deposition over the United States (see Figure 3.20). The meteorology and Hg emission inventory employed in each of the simulations were identical. The first plot (Case 1) shows the model result using GEM oxidation by OH (8.7×10^{-20} cm^3/molec/s) and O_3 (3.0×10^{-20} cm^3/molec/s), this is the scheme implemented in most models. The other subplots show the results obtained when there is no oxidation by OH (Case 2), no oxidation by O_3 (Case 3), no oxidation by either OH or O_3 (Case 4), using a higher kinetic constant for the O_3 oxidation pathway (7.5×10^{-19} cm^3/molec/s) (Case 5), assuming that there is no HgII reduction by aqueous HO_2 (Case 6), and finally no reduction by aqueous HO_2 and no gas phase oxidation by OH (Case 7). As seen in Figure 3.20, removing the OH oxidation mechanism results in a more significant decrease in wet deposition (Case 2) than when the O_3 oxidation mechanism is removed (Case 3), indicating that OH is the dominant oxidant of GEM in the model. Removing both oxidation reactions illustrates the Hg wet deposition which is the direct result of anthropogenic emissions (Case 4). Implementing the higher rate constant for the GEM–O_3 reaction causes much greater wet deposition (Case 5). Removing the aqueous reduction of HgII by HO_2 results in unreasonably high wet deposition (Case 6), and also causes rapid Hg depletion in the gas phase. Case 7 shows that reduction of HgII by HO_2 proceeds more rapidly in the model than GEM oxidation by OH. The magnitude of uncertainty in total wet deposition in the modelling

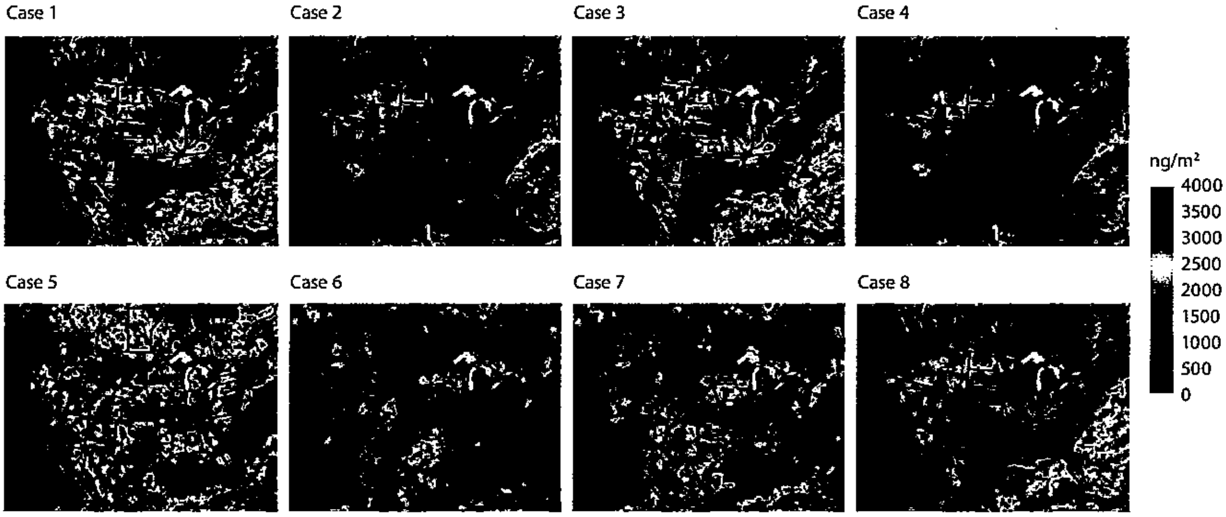


Figure 3.20 Impact of mercury chemistry uncertainty on the simulated monthly mercury wet deposition for the United States in July 2001. The graphic shows eight simulations - see the main text for details. Source: adapted from Travnikov et al. (2010) (cited in: Pirrone and Keating, 2010).

domain, (using Case 1 as the reference simulation) ranges from -50% to +300%. Atmospheric oxidation of GEM is the most important factor determining Hg deposition fluxes in regions far from anthropogenic sources. Improved experimental data addressing these kinetic and product uncertainties would greatly improve model performance in simulating both dry and wet deposition.

3.7.5 Development of process parameterisations

Emissions of GEM from natural processes (re-emission of legacy Hg or primary geogenic emissions) are estimated to be similar to or greater than current anthropogenic emissions, hence their importance to atmospheric Hg models. Traditionally, Hg models have parameterised deposition and surface evasion as independent processes. However, dynamic coupling of Hg exchange at terrestrial and aquatic surfaces is needed to assess the possible impact of changes in anthropogenic emissions or environmental factors such as climate change on the global Hg cycle. Bash (2010) developed and tested a parameterisation for the bi-directional exchange of Hg for the CMAQ (Community Multiscale Air Quality) model that depends on the Hg concentrations in air and surface media. The GEM air-surface exchange was modelled as a function of a dynamic compensation point, which depends on the sources and sinks of GEM in vegetation and soil. This author found that for July, using dynamic bi-directional Hg exchange resulted in an estimated 8.5% of total Hg deposited to terrestrial systems and 47.8% of total Hg deposited to aquatic systems being re-emitted as GEM. Simulations without dynamic bi-directional Hg exchange gave corresponding values of 70.4% and 52.5%. The evasion rates from bi-directional surface Hg exchange were in better agreement with recent estimates of Hg cycling using stable isotopic mass balance experiments.

Simultaneous evaluation of three main atmospheric Hg species: GEM, GOM, and $PBM_{2.5}$, has been limited by lack of ambient measurement data. Holloway et al. (2012) evaluated GEM, GOM, and $PBM_{2.5}$ simulated by CMAQ-Hg, in the Great Lakes Region, at both a rural and urban site. Ambient Hg exhibited significant biases at both sites. They found GEM to be too low in CMAQ-Hg, with the model showing a 6% low bias at the rural site and a 36% low bias at the urban site; whereas oxidised Hg (GOM, $PBM_{2.5}$) was over-predicted by the model, with annual average biases of over 250%. Sensitivity simulations to isolate background inflow from regional emissions suggested that oxidation of imported GEM dominates model estimates of GOM at the rural study site (91%), and contributes 55% to the GOM at the urban site. Their analysis suggested that GEM oxidation rates may be too high in the model, and that the emission ratio of GOM to GEM in urban areas may be inaccurate. These uncertainties in the model have significant implications for estimates of the importance of boundary inflow and regional contributions to local deposition. The authors concluded that Hg chemistry mechanisms and speciation need to be better constrained in order to utilise the model for Hg source attribution studies.

3.8 Conclusions

3.8.1 New findings on atmospheric pathways, transport and fate

It is clear that over the past few decades, and particularly in recent years, much progress has been made in the effort to better understand the sources, chemistry, transport, and deposition of atmospheric Hg. Research studies around the world have provided a better understanding of the relative importance of natural and anthropogenic emission sources, and have expanded the spatial and temporal coverage of atmospheric Hg measurements, which has supported the development and validation of both regional and global atmospheric Hg models. The ever increasing amount of atmospheric and deposition data available is providing more constraints on the rates of processes involved in the atmospheric Hg cycle. Advances in modelling are beginning to permit the linking of atmospheric, ocean and terrestrial models and to tentatively suggest relationships between atmospheric deposition and ecosystem/human exposure to MeHg. It is however very early days from this point of view.

A major accomplishment in the past two years has been the initial development of a concerted international effort to monitor the concentrations and speciation of atmospheric Hg through the GMOS project. The continued efforts of this programme in close cooperation with existing national and regional monitoring programmes will increase the extent of atmospheric and deposition measurements at remote global locations, particularly in the southern hemisphere. The improved spatial and temporal coverage of Hg measurements, following existing standard operating procedures, will provide the data and information for model validation, and for accurate future predictions of the impact of changing Hg emissions on terrestrial and aquatic ecosystems. The continued development and expansion of ground-based measurements is needed in order to more clearly detect changes in atmospheric Hg concentration over time and across the globe. This effort must be approached from a global perspective with collaboration and participation of existing monitoring programmes and networks so as to benefit from existing techniques and collectively improve the approaches to quantifying atmospheric Hg. In reality, the current spatial measurements coverage is insufficient to detect spatial and temporal trends in atmospheric Hg concentration, or to validate regional and global-scale Hg models; however, with the ongoing global-scale measurement expansion, this situation is expected to greatly improve and it will become possible to address these important scientific and policy questions.

3.8.2 Research gaps and areas for future studies

An important attempt is underway through the development of GMOS to develop a globally coordinated monitoring plan which is aimed to fill gaps in terms of monitoring capability in the southern hemisphere, and to establish close cooperation with existing regional and national monitoring networks and programmes. In addition to routine, long-term monitoring campaigns, there is also a need to support coordinated studies of Hg in the upper troposphere through high-altitude and aircraft measurements so as to better understand the vertical distribution of Hg species in the troposphere, as well as long-range Hg transport and source-receptor relationships. An improved understanding of the vertical distribution of atmospheric Hg species is needed for validating regional and global-scale models. New measurement and modelling studies that examine key physical and chemical processes related to global transport and Hg cycling are also needed. This could involve process-based measurements, new monitoring or analytical techniques, and model simulations that examine different chemical scenarios. Continued model development and execution of advanced process-based field experiments can be used to ensure that the models are correctly parameterised. These types of study would also allow improved agreement between models and between model output and experimental data.

More specifically, there are a number of chemical and physical processes that are not well understood, but if they could be investigated more thoroughly it would become possible to improve the chemistry and other parameters in existing Hg models. For example, the chemical form of GOM is not fully understood. Understanding the chemical composition of oxidised Hg compounds is critical to improving model chemistry. Similarly, the redox reaction rates and temperature-dependent rate constants for Hg with atmospheric oxidants also need to be better understood to improve model performance.

Finally, whole-ecosystem studies of Hg are needed to better understand Hg biogeochemical cycling. The link between atmospheric Hg deposition, its methylation, and its eventual uptake by living organisms is also an important area for further investigation. A better knowledge of processes that affect the exchange of gaseous Hg species at ecosystems' interfaces (air-water / -soil / -vegetation) would allow a better parameterisation of these processes in Hg cycling models leading to a better qualified uncertainty estimate of exchanged Hg fluxes.

To summarise:

- There is a need to coordinate activities at the global level to ensure that future research provides the maximum benefits in terms of assessing global and regional trends in Hg concentration in different environmental compartments, including biota.
- The current level of measurements and evaluation is inadequate for determining the extent of temporal and spatial changes in atmospheric Hg concentrations. There is a need to coordinate activities at the global level, including leveraging existing regional networks where investments have already been made.
- There is a need for a permanent global monitoring network (such as that which could be built through the GMOS initiative) to ensure that relevant information is obtained that can also be used for model testing and evaluation.
- In terms of long-range transport and source-receptor relationships, there is a need to facilitate coordinated upper tropospheric studies to better understand the vertical distribution of Hg species in the troposphere. This information is needed to help validate regional and global scale models and reduce the uncertainty in their predictive capabilities for different policy scenarios.

- More investigation, using measurements and models, is required for different key processes related to global transport and cycling of Hg. Model development and focused process studies must continue to be expanded and enhanced to ensure that the models are correctly parameterised and that there is agreement between individual models and between model output and experimental data. Without accredited models, it is difficult to make the pertinent forecasts and scenario predictions that are crucial to the development of sound management strategies for the control and mitigation of the current global Hg problem.
- The chemical form of GOM is not actually known. It is operationally defined as oxidised Hg compounds, but what those compounds are is not well understood.
- Redox reaction rates for Hg with atmospheric oxidants need further investigation. There is still no consensus on which oxidants are important, although recent studies suggest that Br (and possibly Br-containing compounds) are a large contributor. More work is needed to understand the relative importance of these redox reactions as well as to determine temperature-dependent rate constants.
- The link between atmospheric Hg deposition, its methylation, and its eventual update by living organisms is an important area for further investigation.
- The parameters which determine the rates of exchange of Hg compounds at air-sea, air-soil, and air-vegetation are not fully understood, but an improved understanding of these parameters is needed in order to improve existing Hg models.

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Lead and co-authors of the sections of Chapter 3 are as follows:

3.1 Introduction *(N. Pirrone)*; 3.2 Atmospheric chemistry *(I. Hedgecock)*; 3.3 Monitoring networks and programmes around the world *(Leads: F. Sprovieri, L. Gratz; Co-authors: X. Feng, N. Pirrone, E. Prestbo)*; 3.4 Atmospheric mercury measurements and trends worldwide *(Leads: L. Gratz , F. Sprovieri; Co-authors: R. Ebinghaus, X. Feng)*; 3.5 High altitude mercury measurements *(Lead: R. Ebinghaus, Co-authors: L. Gratz, D. Jaffe, F. Sprovieri)*; 3.6 Global mercury modelling *(Lead: O. Travnikov; Co-author: I. Hedgecock)*; 3.7 Regional mercury modelling *(Lead: A. Dastoor; Co-author: I. Hedgecock)*; 3.8 Conclusions *(Lead: Nicola Pirrone; Co-authors: L. Gratz, I. Hedgecock, S. Cinnirella, F. Sprovieri).*

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4. Global Releases of Mercury to Aquatic Environments

Authors: David Kocman, Milena Horvat, Simon Wilson

Contributors: Peter Outridge, Kevin Telmer

4.1 Introduction

Most previous global mercury inventories have only addressed Hg emissions to the atmosphere; releases to aquatic environments have been largely neglected. The results presented here thus represent a first attempt at producing an inventory of Hg releases to aquatic environments on a global scale, taking into account Hg released from anthropogenic and natural sources, as well as sources associated with previously accumulated Hg remobilised from terrestrial to aquatic systems.

The main focus of this chapter is on Hg released to aquatic systems from anthropogenic sources. Natural sources are also considered in order to establish the relative contribution of the anthropogenic component. In the inventory estimates presented here, it is important to distinguish the **direct current releases** of Hg to aquatic systems (i.e., Hg discharged directly into water bodies such as oceans, rivers and lakes) from the more general **inputs** of Hg to water bodies via other pathways, such as atmospheric deposition of Hg to ocean surfaces, or to soils that are subsequently washed into river systems, or riverine inputs of Hg to oceans. One reason for distinguishing between the two categories of input is to avoid double counting current anthropogenic releases.

Two types of anthropogenic sources are considered here: (i) point sources where anthropogenic activities discharge Hg-containing wastes (intentionally or unintentionally) directly to water bodies, and (ii) diffuse releases of Hg through its remobilisation from contaminated surfaces surrounding sites where Hg was used or was/is present in a range of products and processes.

For some sources of Hg to aquatic ecosystems, a lack of detailed information prevents reliable quantitative estimates of Hg release and these sources can only be addressed qualitatively. These sources include land management practices such as deforestation and agriculture, offshore activities, and the use and consequent release of Hg in artisanal and small-scale gold mining (ASGM).

In contrast to Chapter 2 (which deals with atmospheric emissions), the numbers presented here do not necessarily correspond to the year 2010. For example, the underlying assumptions for estimating Hg releases from diffuse sources are based on average annual long-term hydro-meteorological conditions, while releases from point sources were derived from atmospheric inventory data for 2010 presented in Chapter 2, using the UNEP Toolkit distribution factors approach.

Knowledge of Hg releases to aquatic environments is extremely important because it is within aquatic environments that inorganic forms of Hg are converted into the more toxic and bioavailable methylmercury (MeHg) form, thus making the Hg available for accumulation and biomagnification within aquatic food webs. Transport of Hg from its source to aquatic environments depends greatly on its chemical form since it is this in combination with site-specific environmental conditions that determines its mobility, reactivity and bioavailability. Such issues are addressed in more detail in Chapter 5. The main focus of the present chapter is a global inventory and quantification of Hg releases to aquatic systems from sources for which sufficient information is available.

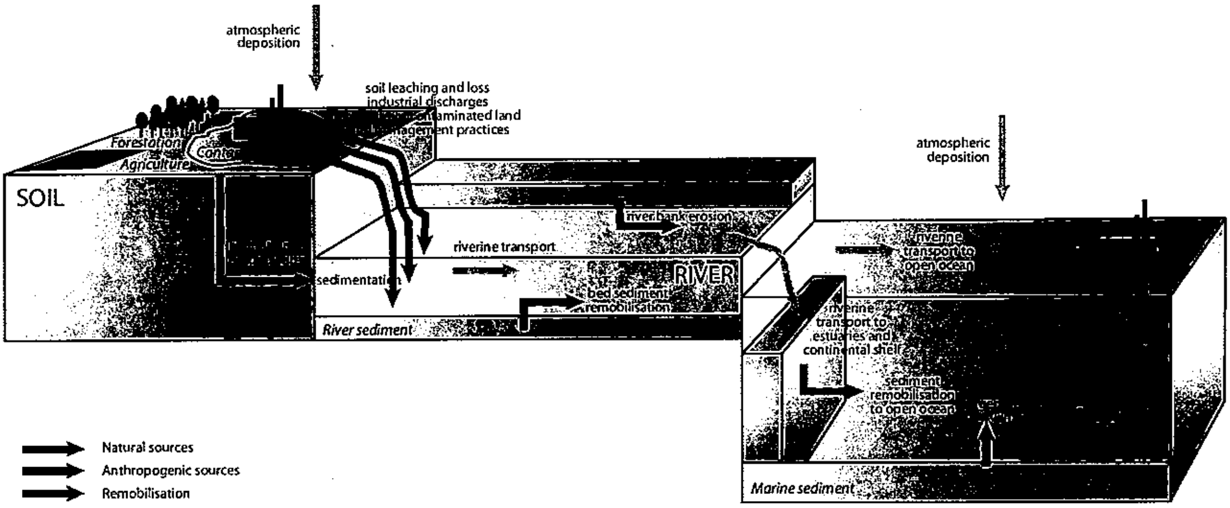

Figure 4.1. Schematic illustration of the major pathways and sources of mercury to aquatic environments.

4.2 Transport pathways for mercury released to aquatic environments

Releases of Hg to aquatic environments can be more complex and difficult to trace in terms of transport routes and source allocation than atmospheric Hg emissions. Figure 4.1 illustrates the major source components and pathways that introduce Hg to aquatic systems.

One of the most important pathways for introducing Hg to aquatic systems is atmospheric deposition. While Hg deposited onto rivers, lakes and oceans enters these systems directly, Hg deposited on land is only partly transported to local aquatic systems (via surface runoff) since a considerable proportion is retained by vegetation and soil. Due to enhanced atmospheric deposition as a result of human activities, the global soil Hg burden has increased considerably since pre-industrial times. Soils can also be significantly enriched in Hg through local releases from industrial installations (see Section 4.3.2.2). This terrestrial Hg pool then serves as a source of Hg for freshwater systems (rivers, lakes and reservoirs) through soil leaching and erosion, with the Hg in both the dissolved and particulate phase. In rivers, Hg associated with particulates is partly sedimented onto the river bed, with the rest (dissolved phases and Hg associated with suspended sediments) transported to downstream environments. During periods of high water flow, this input is enhanced due to river bank erosion and remobilisation of Hg previously deposited with bed sediments. Rivers are an important transport pathway since they convey Hg from one point to another. Ultimately, rivers carry Hg to the marine environment. There, only a small proportion of the total riverine load directly reaches the open ocean, as the majority is deposited in estuaries and on the continental shelf (from where the slow but continuous remobilisation of dissolved and particulate Hg takes place). Exploration and exploitation activities offshore and in coastal waters (such as oil drilling and dredging of bottom sediments etc.) can also contribute Hg directly to the open ocean.

An overall global Hg budget (atmospheric emissions included) based on recent modelling work is discussed in detail in Chapter 1. In order to provide context for the present discussions, a short summary of the global Hg cycle relevant for Hg releases to the aquatic environment is given here based on the most recent data presented by Mason et al. (2012) and references therein. At the global scale, the most recent total atmospheric deposition of Hg (comprising Hg from natural and anthropogenic sources) was estimated at 3200 t/y to land and 3700 t/y to oceans. However, a large proportion of the Hg deposited to both the land and oceans is re-emitted to the atmosphere. Various global models of Hg cycling imply annual (re-)emissions to air from soils and oceans of 1700–2800 t/y and 2000–2950 t/y, respectively. At coastal sites, riverine fluxes can also be important. Estimates of total global river discharges of Hg to estuaries are large (>2800 t/y), but only a small proportion of this Hg is transported to open ocean regions (~380 t/y).

As is the case for Hg emissions to the atmosphere, Hg released to and transported within and between aquatic systems comes from a variety of sources and it is not always possible to determine the origin of the Hg. For the purposes of this study, three types of source are distinguished: new (current) releases from **natural** sources, new (current) releases from **anthropogenic** sources, and **remobilisation** of previously deposited and accumulated Hg (see Figure 4.1).

- Natural sources comprise: (i) Hg released to local aquatic systems from terrestrial surfaces due to its natural (geogenic) occurrence in the earth's crust via leaching, runoff and erosion processes; and (ii) submerged hydrothermal venting. This topic is discussed in Section 4.3.1.
- Anthropogenic sources represent Hg released to aquatic systems as a result of current human activities due to the use and/or presence of Hg in a variety of products and processes (primary and secondary anthropogenic sources are discussed in Chapter 2). These sources comprise: (i) Hg released with the water effluents leaving production sites/plants where Hg is intentionally used (e.g., ASGM, various industrial and chemical processes, production of Hg-containing products, offshore activities); and (ii) leaching from solid waste disposal sites associated with both the unintentional and intentional presence/use of Hg. This topic is discussed in Section 4.3.2.1.
- Remobilisation comprises the release of Hg previously deposited to or accumulated in various environmental compartments by human activities. These are the result of natural processes augmented by anthropogenic activities and include: (i) enhanced atmospheric deposition of Hg as a result of anthropogenic activities (see Chapter 3 for details); (ii) leaching and erosion of Hg-contaminated surfaces; (iii) river bank erosion, and resuspension of river bed sediment and sediment accumulated at coastal sites; and (iv) enhanced Hg releases as a result of various land and water management practices (e.g., agriculture, forestation, dam construction, sediment dredging). These sources can be of local importance only or dispersed over large areas, such as river catchments and contaminated coastal areas. This topic is discussed in Section 4.3.2.2.

4.3 Releases of mercury to aquatic environments

4.3.1 Releases from natural sources

This section discusses inputs of Hg to aquatic systems due to its natural occurrence in terrestrial environments via leaching, runoff and erosion processes; and releases of Hg from undersea hydrothermal vents to open oceans.

Mercury is drained into seas and oceans from the whole continental area, which makes assessment of the relative contribution from natural sources difficult. For the assessment of Hg fluxes from terrestrial environments to rivers and further to seas and oceans, a good knowledge of the spatial distribution of Hg content in soils and rivers is needed, along with site-specific hydro-meteorological and land cover conditions that drive erosion processes. It has been estimated that the total natural (pre-industrial) global soil Hg burden is of the order of 10^6 t for the top 15 cm of soil and that human activities have enhanced this burden by approximately 15% (Selin, 2009). Similarly, Smith-Downey et al. (2010) found that the pre-industrial content of organically bound Hg in soils was 200 000 t globally and that organic soils have stored ~20% of anthropogenic Hg emissions since 1840.

Here, an attempt was made to reconstruct global inputs of Hg to river systems from natural sources only. Two different approaches were used to estimate the natural component of these releases, using different assumptions, as follows. In the first approach, natural annual fluxes of Hg are assumed to be in the range 1–3 $\mu g/m^2/y$, as reported in the literature for various remote and pristine environments (see Grigal, 2002). Applying this range over the total area of the Earth's land surface (~1.5×10^8 km^2 including endoreic regions) results in 150–450 t of annual Hg input to aquatic systems. In the second approach, modelled river sediment fluxes were combined with the Hg content of the surrounding soils, based on the International Satellite Land Surface Climatology (ISLSCP) Initiative II GIS data (Ludwig et al., 2011a). Values of 40±20 ng/g were chosen for Hg soil/sediment concentrations, which covers the range usually reported for background values. This is clearly an oversimplification, as the actual global spatial distribution of Hg naturally present in soils and streams is much more complex and depends on factors such as soil organic carbon content, atmospheric deposition etc.; however it serves the purpose for a relative comparison of natural and anthropogenic sources. In this way, values were obtained that were similar in magnitude but somewhat larger than with the first approach: ~320–960 t (average 640 t) of annual Hg input. The highest natural Hg fluxes to local aquatic systems occur at sites with high erosion rates and consequently higher sediment yield: mountainous regions with steep slopes and a humid climate that enhance erosion processes. In these areas, fluxes can exceed tens or even hundreds of g Hg/km^2 (Figure 4.2). It should be noted that many of these sites coincide with the global distribution of Hg mineral belts and tectonically active areas where soils can be naturally enriched in Hg, resulting in locally elevated inputs to local streams (e.g., the Mediterranean basin, Southeast Asia, and mountainous areas of the Pacific mineral belt).

Hydrothermal vents are an important natural source of Hg for open oceans, most of them being located along the mid-ocean ridges. Figure 4.2 shows the locations of 355 hydrothermal vents, obtained from the VENTS Program (online at: www.pmel.noaa.gov/vents/index.html). Globally, inputs of Hg from hydrothermal vents are estimated to be <600 t/y (Lamborg et al., 2006; Mason et al., 2012). These sources can be of paramount importance especially in geotectonically active areas and semi-enclosed basins such as the Mediterranean Sea (Rajar et al., 2007).

4.3.2 Releases from anthropogenic sources

This section addresses Hg releases to aquatic systems as a result of human activities. The first part (Section 4.3.2.1)

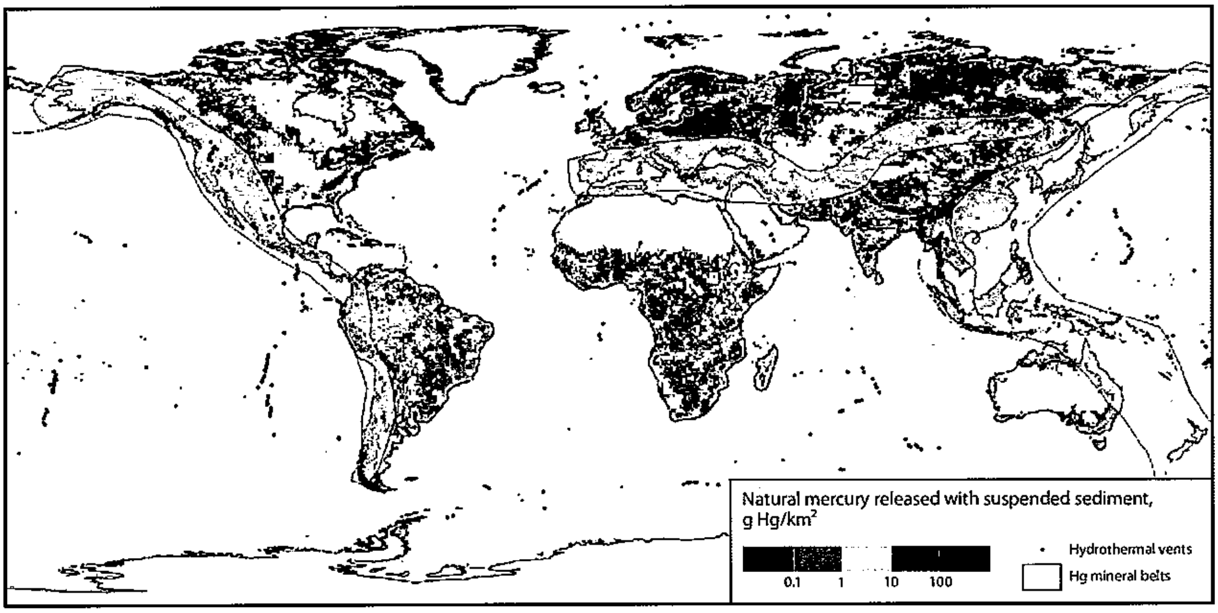

Figure 4.2. Natural mercury fluxes (per 0.5 grid cell) associated with suspended material (based on ISLSCP data (Ludwig et al., 2011a) obtained from: http://dx.doi.org/10.3334/ORNLDAAC/1019) in river systems. The global distribution of mercury mineral belts (modified from Gustin et al., 1999 and Rytuba, 2003) and hydrothermal vents (locations obtained from: www.pmel.noaa.gov/vents/index.html) are also shown.

covers Hg releases from point sources. Due to the differences in approaches used, these sources are discussed separately for the various industrial installations (chlor-alkali industry, oil refining, non-ferrous metals processing), ASGM, and offshore oil and gas operations. In the second part (Section 4.3.2.2) diffuse releases of Hg to aquatic systems are discussed, including riverine inputs to coastal environments, remobilisation from contaminated sites, and releases as a consequence of land and water management practices.

4.3.2.1 Releases of mercury to aquatic systems from point sources

4.3.2.1.1 Releases of mercury from industrial installations

In general, releases of Hg to aquatic environments from anthropogenic point sources are very poorly documented, and unlike the case for air emissions, no recent global inventories of anthropogenic Hg releases to water exist. Some (European) countries report estimates of Hg releases to water under international programmes, such as OSPAR (www.ospar.org) and HELCOM (www.helcom.fi), but this is mainly for the purpose of deriving estimates of inputs (via riverine inputs and direct discharges) to the marine areas covered by these Conventions. Other countries have delivered national estimates of Hg releases to water (in different years) to UNEP through national Hg release inventories prepared using the UNEP Toolkit [online at: www.unep.org/hazardoussubstances/Mercury/Informationmaterials/ReleaseInventories/tabid/79332/Default.aspx]. Mercury releases to water from specific industrial

Table 4.1. UNEP Toolkit distribution factors used for calculation of releases from point sources. Source: UNEP (2011a,b).

NFM: non-ferrous metal production; CAP: Chlor-alkali production with Hg-technology.

Source category	Distribution factors		
	Air	Water	Land
Oil refining	0.25	0.01	-
NFM-Cu	0.1	0.02	0.24
NFM-Pb	0.1	0.02	-
NFM-Zn	0.1	0.02	-
NFM-Al	0.15	0.1	-
NFM-Hg	0.25	0.06	0.69
NFM-Au	0.04	0.02	0.9
CAP	0.1	0.01	0.01
Other waste	0.1	0.1	0.8

Table 4.2. Calculated annual releases of mercury to aquatic systems by sub-region and for various sectors (data in tonnes).

NFM: non-ferrous metal production; CAP: Chlor-alkali production with Hg-technology; ASGM: Artisanal and small-scale gold mining; EU27: The 27 EU Member States.

Sub-region	Oil refining	NFM-Cu	NFM-Pb	NFM-Zn
Australia, New Zealand & Oceania	0.003 (0.001–0.005)	0.16 (0.06–0.81)	0.03 (0.01–0.05)	0.62 (0.37–0.69)
Central America and the Caribbean	0.004 (0.002–0.006)	0.43 (0.21–1.83)	0.04 (0.02–0.07)	1.08 (0.55–2.25)
CIS & other European countries	0.043 (0.019–0.071)	2.77 (0.99–13.9)	0.07 (0.02–0.15)	1.94 (0.74–4.44)
East and Southeast Asia	0.381 (0.172–0.629)	6.45 (2.38–31.8)	0.69 (0.24–1.42)	9.29 (5.21–14.9)
EU27	0.081 (0.039–0.134)	1.11 (0.40–5.58)	0.05 (0.02–0.10)	1.13 (0.46–2.56)
Middle Eastern States	0.007 (0.003–0.011)	0.53 (0.19–2.66)	0.01 (0.002–0.01)	0.14 (0.05–0.33)
North Africa	0.007 (0.003–0.012)	–	0.02 (0.01–0.05)	0.11 (0.04–0.27)
North America	0.072 (0.034–0.119)	0.24 (0.09–1.17)	0.01 (0.003–0.01)	0.07 (0.04–0.58)
South America	0.012 (0.005–0.020)	3.72 (1.33–18.6)	0.01 (0.004–0.02)	0.95 (0.36–2.30)
South Asia	0.028 (0.013–0.046)	2.24 (0.80–11.2)	0.03 (0.01–0.07)	2.16 (0.81–5.31)
Sub-Saharan Africa	0.001 (0.001–0.002)	1.11 (0.40–5.57)	–	0.50 (0.19–1.24)
Total	0.639 (0.293–1.055)	18.8 (6.83–96.16)	0.95 (0.35–1.97)	18.0 (8.83–34.9)

[a] Releases to land and water as discussed in Section 4.3.2.1.2.

facilities are also partly included in databases/registers such as North American Pollutant Releases and Transfers (NAPRT, comprising Canada's National Pollutant Release Inventory [NPRI], Mexico's Registro de Emisiones y Transferencia de Contaminantes [RETC], and the United States' Toxics Release Inventory [TRI], online at: www.cec.org); the European Pollutant Release and Transfer Register (E-PRTR, covers the 27 EU Member States as well as Iceland, Liechtenstein, Norway, Serbia and Switzerland, online at: http://prtr.ec.europa.eu/); and the Australian National Pollution Inventory (NPRI, online at: www.npi.gov.au). On a sector basis, efforts have been made to compile information on releases from specific activities. For example, OSPAR reporting also includes annual reporting (most recently for 2009) of releases of Hg from the chlor-alkali industry (OSPAR, 2011).

The approaches and underlying assumptions used in the preparation of these inventories and release estimates differ from country to country and different databases/registers cover different industry sectors and economic activities, which makes comparison of various inventories difficult. Moreover, reporting requirements are subject to different thresholds and often lack documentation and transparency/traceability with regard to the basis for the estimates (see discussion in Chapter 2), although the UNEP Toolkit approach (UNEP, 2011a,b) attempts to address these issues.

In the absence of detailed information necessary to prepare a comprehensive inventory of releases to water, and in order to produce a first-order global inventory of anthropogenic Hg releases to water, a crude approach combining the atmospheric inventory results presented in Chapter 2 of this report with the information and assumptions included in the UNEP Toolkit approach has been employed. This approach adopts the (default) distribution factors that are applied in the UNEP Toolkit to 'distribute' total Hg releases to the environment between air, water and land (Table 4.1), and uses these factors to calculate corresponding releases to water for the air emissions developed in Chapter 2 of this report. It should be recognised that this is a very coarse approach, with large associated uncertainties. Namely, the uncertainties related to atmospheric emission estimates associated with the activity data used, emission factors and assumptions made regarding applied technologies (see Chapter 2 for details) are compounded by additional uncertainties related to the validity and utility of the Toolkit distribution factors. It should also be noted that this approach has the potential to miss releases to water that are associated with activities where air emissions are insignificant (and thus there are no corresponding emissions included in the air emissions inventory).

Using the approach described above, anthropogenic releases to water have been calculated, and the results by sub-regions for various sectors are given in Table 4.2. These

NFM-Al	NFM-Hg	NFM-Au	CAP	Other waste	ASGM[a]
0.21 (0.08–0.44)	–	6.31 (0.04–16.4)	–	0.47 (0.13–1.60)	3.50
–	–	1.95 (0.02–4.48)	0.06 (0.02–0.12)	3.40 (0.88–11.2)	6.45
0.94 (0.37–1.95)	0.53 (0.31–0.81)	8.04 (0.06–20.9)	1.12 (0.39–2.17)	7.00 (1.81–23.9)	10.3
1.30 (0.52–2.45)	2.27 (1.32–3.44)	11.5 (0.08–29.9)	0.12 (0.04–0.24)	34.3 (8.67–118)	454
0.03 (0.01–0.06)	–	0.14 (0.001–0.36)	0.65 (0.23–1.26)	4.48 (0.93–16.2)	–
0.05 (0.02–0.10)	–	0.25 (0.002–0.66)	0.22 (0.08–0.42)	4.44 (1.12–14.8)	–
0.01 (0.003–0.02)	0.02 (0.01–0.02)	0.06 (0.0004–0.16)	0.13 (0.05–0.26)	2.37 (0.62–7.59)	–
0.12 (0.04–0.24)	–	0.82 (0.01–2.13)	0.11 (0.04–0.21)	4.57 (1.10–16.5)	–
0.21 (0.08–0.43)	–	7.66 (0.06–19.6)	0.25 (0.11–0.42)	7.53 (1.96–25.6)	313
0.31 (0.12–0.64)	–	0.08 (0.001–0.20)	0.16 (0.06–0.31)	16.6 (3.94–58.8)	0.37
0.09 (0.06–0.12)	–	11.9 (0.10–28.8)	0.02 (0.01–0.04)	4.18 (1.03–13.9)	93.7
3.27 (1.31–6.45)	2.82 (1.64–4.28)	48.7 (0.36–124)	2.84 (1.02–5.47)	89.4 (22.2–308)	881

results can be compared with release estimates obtained using independent approaches and assumptions. For example, according to the NAPRT database where North American facilities releases are reported, total on-site surface water discharges in 2009 for all industry sectors included in the database is ~5 t/y. This is very similar to ~6 t/y calculated for North America according to the Toolkit approach. However, in this case it should be mentioned that the sectors included in the NAPRT database differ from the sectors included in the present calculations and, for US air emissions at least, NAPRT-based totals are lower than those reported under the US national emission inventory (NEI). Similarly, the OSPAR Commission reported 0.14 t of Hg released with waste water from 29 chlor-alkali plants located within the OSPAR region in 2009 (OSPAR, 2011e). Applying this value to 39 chlor-alkali plants still using Hg cell technologies in the 27 EU Member States (UNEP, 2011) would result in an annual release of 0.18 t from this sector. This is similar in magnitude but somewhat lower than the calculated 0.65 t/y using the Toolkit approach. For the oil refining sector, a wide range of values for Hg releases to water are reported for different regions in various databases/registers: for example, 0.03–0.36 kg/facility in 2011 (NPRI, Australia), 0.2–1.28 kg/facility in 2010 (NPRI, Canada) and 645 kg from 17 mineral oil and gas refineries in Europe in 2010 (E-PRTR). Measurements implemented within the framework of the EU research project BIOMERCURY (Horvat et al., 2007) revealed that in an oil refinery in central Europe the concentration of Hg in purified waste water was 2.1 μg/L, while the concentration in waste water treatment sludge reached over 230 μg/kg. The mass balance indicated that about 16% of Hg entering the oil refinery was discharged by waste waters (Horvat et al., 2007). Considering these ranges and applying a rather conservative value of 0.5 kg/y of Hg released from over 650 oil refineries globally (OGJ, 2006) would approximate to 0.3 t/y, which is similar to the 0.6 t/y using the Toolkit approach.

It should be noted, however, that Hg releases to water might also be significant for some sectors currently not covered by the UNEP Toolkit as no distribution factors exist for these categories that would enable calculation of the releases. For example, out of 9.29 t of Hg released to water from 423 facilities reported in E-PRTR in 2010, 6.79 t is attributed to releases from urban waste-water treatment plants. Considering the large number of these facilities, the large volumes of water used in the process and the fact that the threshold for Hg releases to water in E-PRTR is set at the relatively high 1 kg/y, actual releases might be significantly higher. Sewage treatment can also be an important sector. Based on Canada's NPRI, 0.14 t of Hg was released to water from 23 sewage treatment plants in 2010.

4.3.2.1.2 Releases due to mercury use in ASGM activities

Environmental impacts due to the Hg use in ASGM activities have been documented in many studies, and a comprehensive review of worldwide ASGM activities was made by Telmer and Veiga (2009). According to most recent estimates, ASGM releases to all environmental compartments averaged 1607 t Hg/y globally (range 910–2305 t/y) in 2011. Of these, on average 55% is released to terrestrial systems, resulting in an input of 881 t/y (range 498–1263 t/y). The ratio between Hg emitted to the atmosphere and that released to terrestrial systems depends on the practices used in ASGM activities. As discussed in Chapter 2 of this report (where methodology used for release estimates is described in more detail), in regions where concentrate amalgamation is practised, 75% of the Hg used is emitted to the atmosphere, whereas localities that practise whole ore amalgamation release a much larger proportion of the Hg to aquatic and terrestrial systems. Based on the knowledge about ASGM practices employed in each country in Table 4.2 these releases are summarised for different sub-regions. The data presented in this table show the total annual amount of Hg released due to its active use in ASGM activities and which accumulates in local rivers, lakes, soils and tailings. However, a proportion of the amount released into these terrestrial ecosystems is later remobilised to the hydrosphere. How much actually enters aquatic environments due to erosion and is further subjected to riverine transport is unknown and hard to establish due to the lack of suitable data. For this purpose, the extent of contamination should be established for each individual site, as well as a good knowledge regarding site-specific hydro-meteorological conditions. However, as ASGM activities are conducted at hundreds of small sites, they cannot be individually identified. Moreover, as these sites are distributed globally in zones with very variable hydro-meteorological conditions, it is reasonable to expect that inputs to local aquatic systems will significantly differ from site to site. Therefore, just to give a rough estimate of the possible global remobilisation of Hg from these sites, a semi-quantitative approach was used. Countries with known ASGM activities were grouped according to their susceptibility to erosion. For this purpose, global composite surface runoff data available in the GIS format were used (Fekete et al., 2000), as runoff is the most important driver of soil erosion. Countries were then classified into three groups: countries with a very dry climate (on average <100 mm surface runoff per year) where aquatic inputs can be considered negligible, countries with a very humid climate (>1000 mm runoff per year) where such inputs can be important, and others that fall in-between these two classes. Using this approach, it was found that most of the countries in the first group are African countries with relatively low production and consequent releases (74 t/y), while many countries in the second group are those with the highest ASGM activity and releases. Among others this includes Colombia, Indonesia, Philippines, Brazil, Guyana, Vietnam, Papua New Guinea, French Guiana, Suriname and Malaysia. Altogether, these countries alone contribute more than 36% (~320 t/y) of global releases to terrestrial compartments from ASGM. Therefore, ASGM can be a very important source of Hg for aquatic systems. However, it should be mentioned that the dominant source of contamination of local aquatic systems is not necessarily the loss of Hg in the gold amalgamation process itself, but the disturbance and mobilisation of large quantities of Hg-rich sediment and floodplain soil during mining operations (sluicing and dredging), as reported for the Tapajos River in the Brazilian Amazon by Telmer et al. (2006).

4.3.2.1.3 Releases associated with offshore oil and gas operations

Globally, most of the offshore oil and gas fields are located in the Persian Gulf/Middle East, North Sea, West Africa, the Gulf of Mexico (US and Mexico), Asia/Australasia, Brazil, China, the Caspian Sea and Russia/Arctic. Offshore production involves 17 000 operating platforms, with more than 400 new production facilities (fixed, floating and subsea platforms) being constructed every year (IFP Energies nouvelles, 2012). During extraction, Hg associated with crude oil and natural gas is released in wastewater streams and in solid waste streams (IKIMP, 2012). These releases vary a lot from site to site and depend on the Hg content in crude oil and gas, and the technology used at individual sites. Sediments adjacent to offshore drilling sites often contain elevated Hg levels due to its association with barite, a common additive to drilling mud (Wilhelm, 2001; Trefry et al., 2002, 2007). Reported Hg concentrations in drilling muds range from 0.05–0.75 mg/kg (Neff et al., 2003; Trefry et al., 2007; IKIMP, 2012 and references therein). Neff et al. (2003) estimated that 153 kg of Hg was discharged to the Gulf of Mexico in 2001 in permitted discharges of drilling muds and cuttings from a total of 900 wells drilled, while the annual release to North Sea sediments in 2010 was estimated at 12–22 kg (IKIMP, 2012). Applying these values to the global number of wells drilled would result in several tonnes of Hg released to the ocean floor due to this activity. However, such a worldwide extrapolation is associated with large uncertainty. For example, in Norway barite was replaced by ilmenite in 2003, resulting in significantly lower Hg releases (<10 kg annually) from drilling operations on the Norwegian Continental Shelf (NCPA, 2011). Moreover, it should be noted that Hg present in drilling muds and cuttings is present primarily as insoluble sulphide, and MeHg concentrations in sediments and marine organisms around drilling sites were found to be comparable with background sites (Neff et al., 2003; Trefry et al., 2007). Another possible release of Hg to local aquatic systems occurs during the production phase when hydrocarbons, natural gas and water phases are separated, especially as most of the produced water originating on offshore platforms is discharged to the ocean (Wilhelm, 2001). Available information on the Hg content of produced water is relatively scarce and there is a wide range of reported values. In the past there was a lot uncertainty associated with these values due to the poorly developed analytical methods with high detection limits (Wilhelm, 2001), resulting in large variations in reported releases. For example, while Wilhelm (2001) reported 0.3 trillion litres of offshore produced water annually discharged within U.S. oil and gas production and uses 1 µg/L for the Hg concentration, which would result in 300 kg/y of Hg discharged, Neff et al. (2003) reported that produced water usually contains less than 0.1 µg/L and that only 3.6 kg/y of Hg is discharged to the U.S. Gulf of Mexico. More recent data from measurements at just over 100 facilities on the UK Continental Shelf revealed mean Hg concentrations of 0.46 µg/L (2008) and 0.94 µg/L (2009), resulting in annual Hg discharges of 91 and 186 kg, respectively (IKIMP, 2012). Similarly, on the Norwegian continental shelf, ~5–17 kg of Hg was discharged annually with produced water in the 2000–2009 period (NCPA, 2011). On the other hand, significantly higher Hg concentrations in the 30–800 µg/L range are reported for offshore platforms in the Gulf of Thailand with associated Hg releases of between 40 and 330 kg/y in the 1991–1996 period (Chongprasith et al., 2001). Taking into account the number of operating platforms globally and the reported releases of Hg, it can be concluded that oil and gas offshore operations are an important source of Hg for oceans. However, due to the lack of data and large variations in reported concentrations, any global quantification of Hg releases from this sector would be associated with too large an uncertainty.

4.3.2.2 Diffuse releases of mercury to aquatic systems

4.3.2.2.1 Riverine inputs to coastal environments

Part of the Hg being drained into local river systems from sources in the catchments is retained in rivers, mostly associated with the bed sediment, while the rest ultimately reaches coastal sites in both the dissolved and particulate phase. The total Hg load entering lakes and oceans depends on the size of the drainage area and the Hg levels in the basin, and can be quite significant also in non-contaminated basins. For example, Carrie et al. (2012) calculated that 4.3 t of Hg is exported each year to the delta from the Mackenzie River Basin, which is the least human-impacted large watershed in the world, and the Hg input is primarily derived from the weathering of sulphide minerals. The OSPAR Commission reported that 306 t of Hg were discharged into the North-East Atlantic area covered by the OSPAR Convention in the period 1990–2002. Of that, 23 t are direct releases to the sea (for example, through pipelines), while the remaining 283 t are contributed by riverine inputs (OSPAR, 2005). Similarly, recent model results revealed that circumpolar rivers and coastal erosion might be the dominant source of Hg (95 t/y) to the Arctic Ocean (Fisher et al., 2012). Almost 500 kg of Hg has been transported to the New York/New Jersey Harbour from various sources in one year, with 67% of the total input from rivers (Balcom et al., 2008). A Hg mass balance was also calculated for the Mediterranean Sea, which is a relatively closed basin where riverine Hg inputs can be extremely important. The total mass of Hg in the water column of the Mediterranean Sea for 2005 was estimated at 1080 t, with the contribution of Hg from rivers ~14 t/y and point sources ~2.5 t/y (Rajar et al., 2007). The importance of riverine inputs of Hg to oceans was also emphasised in a recent study by Soerensen et al. (2012) where it was hypothesised that the historical decline of Hg in the North Atlantic Ocean could be attributed to decreased riverine and wastewater inputs at ocean margins.

In addition to terrestrial surfaces being drained to seas and oceans, significant parts of the world's continents belong to so-called endoreic regions. These are regions where rivers flow into internal basins (i.e., without outflow) because of a combination of climatic aridity and continental morphology, and cover 10% of the surface of the continents (Feller, 2010). Some of the most important such regions are Lake Eyre in Australia, the Okavango river system in Africa, the Tarim basin in China, the Great Basin in the United States, Altiplano in South America and the Aral Sea and Caspian Sea drainage in central Asia (Feller, 2010). Significant amounts of Hg can end up in these lakes. One such well known and well studied example is Hg contamination in the Laurentian Great Lakes region in North America, where contamination represents a combination of historical loadings from industrial activities in the drainage area of the lakes as well as enhanced atmospheric deposition in the area (Marvin et al., 2004; Wiener et al., 2012). Lakes with Hg point sources in the drainage area can also be significantly affected. One such example is Clear Lake in the USA, where ~100 t of Hg was deposited into the lake's ecosystem from the Sulfur Bank mercury mine (Suchanek et al., 2008). Sediments trapped in such closed systems act as a sink for Hg from which it can be remobilised by resuspension and represent important sites for the production of MeHg (Ullrich et al., 2001) that affects fish and wildlife.

An approach similar to that of Sunderland and Mason (2007) was used for estimating global Hg inputs to oceans from rivers in both the particulate and dissolved phases. Calculations are based on the long-term average sediment loads and freshwater discharges obtained from ISLSCP Initiative II data (Amiotte-Suchet and Probst, 1995; Ludwig et al., 1996; Hall et al., 2006), available in GIS format (Ludwig et. at., 2011b). In this database, sediment yields were predicted by correlating them with the products of hydroclimatic, geomorphological, and lithological factors, while drainage intensity was obtained from Korzoun et al. (1977) and Ludwig and Probst (1998). River Hg concentrations for different ocean basins were adopted from Sunderland and Mason (2007) and references therein. As seen in Table 4.3, the average total annual input of Hg to the coastal sites is estimated at 2473 t. Of that, the majority (95%) is attributed to Hg associated with suspended sediments, the rest being in the dissolved phase. These total inputs are large and in agreement with the numbers reported by Sunderland and Mason (2007), but only a small proportion of (~10%) this Hg is transported to open ocean regions (Mason et al., 2012), the rest being deposited around river mouths and on continental shelves (Cossa et al., 1997; Sunderland and Mason, 2007). Mercury fluxes to the oceans are highest around the mouths of major world rivers and at sites where sediment export is increased due to site-specific hydro-meteorological conditions (Figure 4.3). Many of these sites are located in tropical and subtropical coastal environments which are especially sensitive to Hg loads (Costa et al., 2012).

4.3.2.2.2 Remobilisation of mercury to aquatic environments from contaminated sites

This section discusses remobilisation of Hg from various contaminated terrestrial environments to local aquatic systems. Here, a contaminated site is defined as a site with elevated Hg content relative to local background, as a consequence of Hg use or its presence in a variety of products

Table 4.3. Global particulate and dissolved river mercury inputs to estuaries.
Hg_P; mercury in the particulate phase; Hg_D; mercury in the dissolved phase.

Ocean basin	Area[a], 10^3 km^2	Sediment[a], Gt/y	Runoff[a], km^3/y	Hg_P[b], ng/g	Hg_D[b], ng/L	Hg_P load, t	Hg_D load, t
Arctic Ocean	16982	0.235	3239	80 ± 40	0.6 ± 0.4	9.40 – 28.2	0.65 – 3.25
North Atlantic	27300	3.600	13484	200 ± 100	3.0 ± 2.0	360 – 1080	13.5 – 67.6
South Atlantic	16959	0.523	5074	200 ± 100	3.0 ± 2.0	52.3 – 157	5.09 – 25.4
Pacific	21025	7.407	13532	120 ± 60	3.0 ± 2.0	444 – 1333	13.5 – 67.9
Indian Ocean	16594	3.556	5166	120 ± 60	3.0 ± 2.0	213 – 640	5.18 – 25.9
Mediterranean Sea	6739	0.708	1087	280 ± 140	0.9 ± 0.6	99.1 – 297	0.28 – 1.68
South of 60° S	728	0.007	162	80 ± 40	0.6 ± 0.4	0.28 – 0.84	0.03 – 0.16
					Range	1179 – 3537	38 – 192
					Average	2358	115
					Sum	2473	

[a] Area of global land surfaces without endoreic regions and regions that are under permanent ice cover, sediment and runoff data obtained from ISLSCP; [b] river Hg concentrations from Sunderland and Mason (2007) and references therein.

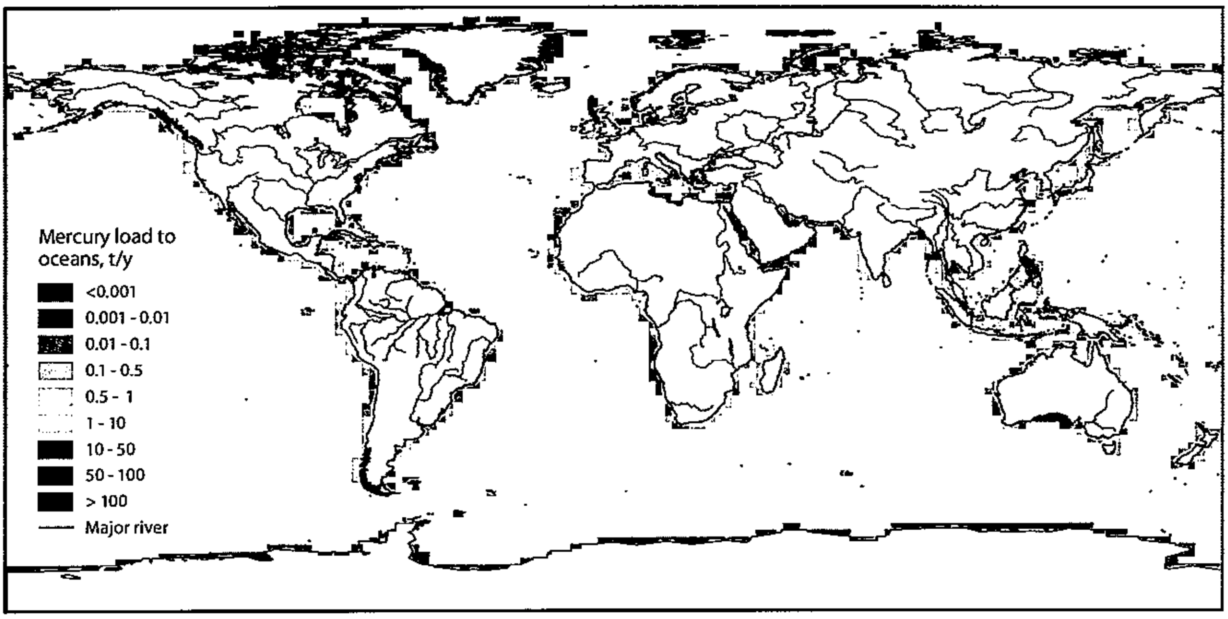

Figure 4.3. Average annual mercury fluxes (per grid cell) to oceans associated with suspended sediments. Source: based on ISLSCP data (Ludwig et. at., 2011b) obtained from: http://dx.doi.org/10.3334/ORNLDAAC/1028

and industrial processes. Depending on the source of Hg, production rate and release pathways at individual sites (direct releases to local terrestrial systems or Hg initially emitted to the atmosphere and then deposited in the surroundings of these sites), these sites can vary greatly in size (from hundreds of square metres to tens of square kilometres). Significant amounts of Hg are known to be transported to marine environments from these sites, especially because a big part of the world's urban and industrial areas are located near the coast. Due to the lack of environmental regulations in the past, at many of these locations, Hg was discharged for decades directly into nearby marine environments. One of the best known examples is Minamata Bay in Japan, where Hg-contaminated effluents were discharged for 30 years from a local acetaldehyde factory, causing the notorious Minamata disease in the local population eating contaminated seafood from the bay (Tomiyasu et al., 2006 and references therein). While the most contaminated sediments were removed from Minamata Bay, 1800 t of Hg are still present in the sediments of the Gulf of Trieste in the Northern Adriatic owing to drainage from the Idrija Hg mine region over the past 500 years. A mass-balance evaluation indicated that ~800 kg of this settled Hg re-enters the water column each year due to resuspension and to diffusion at the sea bottom-water interface (Rajar et al., 2004). Similarly, more than 140 t of Hg have accumulated in San Francisco Bay due to the historic mercury and gold mining activities in California (MacLeod et al., 2005). Since 1956, Hg has been continuously introduced into northern Haifa Bay in Israel from a nearby chlor-alkali plant. The total Hg input from this plant to the bay is estimated at ~22 t (Herut et al., 1996).

Inputs to aquatic environments from contaminated sites were calculated based on a recently constructed geo-referenced database of the global distribution of contaminated sites (Kocman et al., 2013). In this database, the following most important categories of Hg sources and/or uses resulting in the occurrence of contaminated sites are included: locations of primary Hg mining, precious metal processing, non-ferrous metal production and various polluted industrial and urban sites. The locations of these sites are shown in Figure 4.4 and the categories briefly described below.

Primary mercury mining: Globally, approximately one million tonnes of Hg was extracted from various ore bodies, mostly in the region of the mercuriferous belts between the Mediterranean and central Asia (Hylander and Meili, 2003). It is believed that only a few percent of all Hg mined has escaped to the atmosphere so far (Hylander and Meili, 2003), the rest being available for remobilisation within the global Hg budget. The amount of Hg released to the environment, including aquatic systems, during mining and Hg ore production depends mostly on the technology used, which has changed considerably over the centuries. Based on the data on Hg production and smelting recovery reported by Kotnik et al. (2005) for the Idrija Hg mine in Slovenia in the period between 1960 and 1995, approximately 70% of total Hg lost into the environment was deposited in landfill as smelting residue, 25% was emitted into the atmosphere by flue gases and the remaining 5% released to the aquatic environment as condensation water. Applying these percentages to historical global Hg production (Hylander and Meili, 2003), results in approximately 175 000 t of Hg ore residues, 62 500 t of atmospheric emissions and 12 500 t of Hg directly released to aquatic systems in the past 500 years. This is clearly an oversimplification and might underestimate past Hg releases, as it is known that recovery of Hg in smelting has changed significantly (from 30% to over 90%) over the centuries (Kotnik et al., 2005).

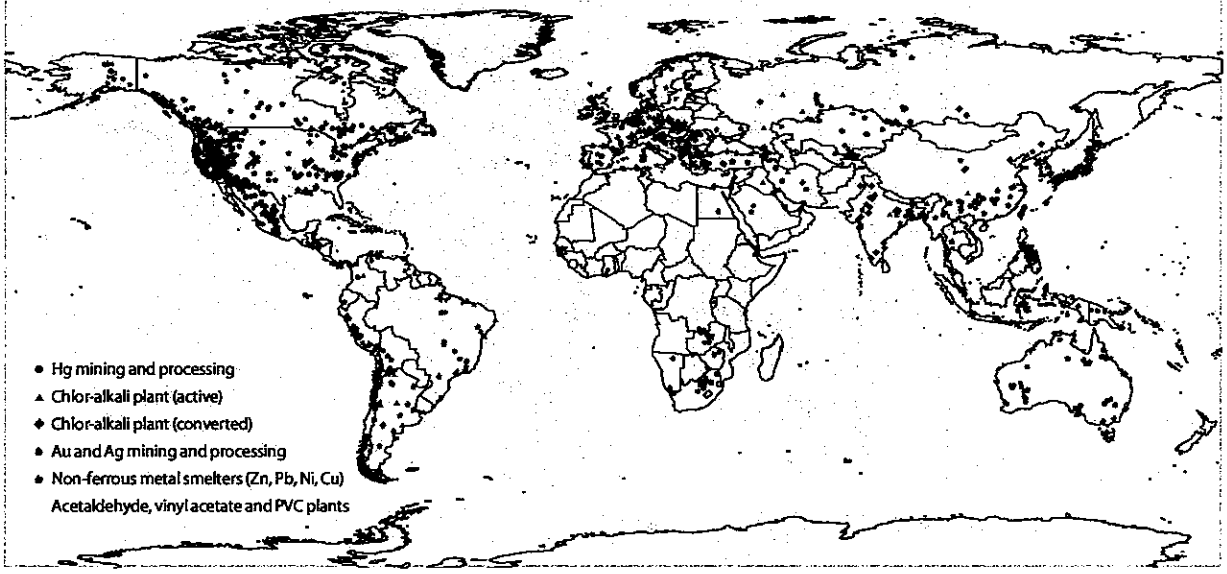

Figure 4.4. Global distribution of mercury-contaminated sites. Source: adapted from Kocman et al. (2013).

Chlor-alkali industry: According to the latest report by industry (UNEP, 2011e) there are approximately 100 active facilities worldwide with industrial Hg cell chlorine capacity. In addition, there are many locations where such facilities were either closed or shifted to Hg-free technology, but still act as a source of Hg to aquatic systems due to improper or inefficient remediation and waste disposal. Due to the large amount of Hg used in this sector, strongly elevated concentrations of Hg in soils can be found in the few kilometre radiuses surrounding these sites (e.g., Biester et al., 2002; Remy et al., 2003; Hissler and Probst, 2006).

Large scale precious metal processing: Historically, approximately half of all Hg mined has been used in gold and silver mining (Hylander and Meili, 2003), mostly in North and South America. It was estimated that total losses of Hg to all environmental compartments were 196 000 t in South and Central America and 61 380 t in the United States (Nriagu, 1994). In addition, due to the co-occurrence of Hg in gold and silver ores, during ore processing new Hg is released to the environment. For the reasons stated in the atmospheric part of this report (see Section 2.2.7), release estimates for this category also have large associated uncertainties.

Non-ferrous metal production: This category covers locations where zinc, copper, lead and nickel ores are processed. Contamination occurs due to the use of thermal methods during processing of these ores that can contain significant amounts of Hg. These locations are known sources of Hg (e.g., Li et al., 2008), but are extremely poorly documented, especially in terms of their surrounding aquatic systems.

Other industrial sites: Within this category are grouped locations of factories of acetaldehyde, vinyl chloride and vinyl acetate which used or may have used Hg as a catalyst. As with chlor-alkali plants, these sites are known sources of Hg pollution that can affect aquatic systems at distances exceeding 200 km (Ullrich et al., 2007).

Mercury input to aquatic systems from these sites depends on the level and extent of contamination, as well as local hydro-meteorological conditions that influence erosion and surface runoff processes. Due to the lack of detailed site-specific data, especially on substrate Hg content, the following approach was used. For each of the contaminated sites (mining and/or processing sites, industries intentionally using Hg as a catalyst), site-specific sediment yields were extracted from the GIS map of fluxes of total suspended solids available within the ISLSCP Initiative II Global Datasets (Ludwig et al., 2011b). Observations made for various case studies reported in the literature were used as the basis for selecting the size of the contributing area and the range of average soil Hg content that can be expected at these sites. In Table 4.4, the results of this approach and the assumptions made within individual contaminated site categories are shown.

4.3.2.2.3 Mercury releases as a consequence of land and water management practices

Agriculture

Historically, pesticides and fungicides containing Hg were widely used in agriculture, making this sector an important source of Hg for aquatic systems (Wang et al., 2004). In the 1960s, 2100 t of Hg were used in agriculture globally (Smart, 1968 in Wang et al., 2004). As far as is known, there are no recent data regarding quantitative assessment of Hg releases from this source. According to the report of the World Health Organization, mercurial compounds were widely used in agriculture through much of the 20th century, and although banned, some use was reported to have occurred in some parts of the world (e.g. Russia, Canada) even over the past decade (WHO, 2010 and references therein). Nowadays, huge amounts of sewage sludge are spread on land for agricultural use. For example, the total quantity (i.e., production) of sewage sludge in the 27 EU Member States is currently estimated at 10.13 million

Table 4.4. Calculated releases to aquatic systems from contaminated sites and assumptions made.

CAP: Chlor-alkali production with Hg-technology.

	Contributing area[a]	Hg soil content, mg/kg	Hg released, t/y
Primary mercury			
large	200 km^2		
medium	100 km^2	0.5 - 2.0	6.66 – 26.6
others	50 km^2		
CAPs	2-3 km radius	0.2 – 0.5	0.09 – 0.48
Non-ferrous metal	2-3 km radius	0.1 – 0.2	0.12 - 0.54
Precious metal			
mining	50-100 km^2	0.5 - 1.0	1.35 – 5.54
processing	2-3 km radius	0.2 - 0.5	
Other industries	2-3 km radius	0.2 – 0.5	0.06 – 0.33
		Total	8.3 – 33.5

[a] The size of the contributing area was selected based on the values used for calculating Hg emissions to the atmosphere from these sites as reported by Kocman et al. (2013).

tonnes (dry solids), and nearly 40% of this total is estimated to be used in agriculture (Milieu, 2010a). The Hg content of sewage sludge recycled to agriculture varies from country to country and ranges between 0.2 and 4.6 mg/kg (Milieu, 2010b). The most recent estimate of Hg introduced into agricultural soils in the EU27 is 4.4 t/y (BIO Intelligence Service, 2012).

Silviculture

Various practices used in forestry disturb the soil and so influence the mobility and availability of Hg for downstream aquatic systems. The increased transport is caused by increased erosion and changed hydrological pathways and yield through the catchment soils. Several studies in Fennoscandia and North America have reported increased transport of Hg and in some cases large increases in MeHg, but the variability in response is large (Bishop et al., 2009; Sørensen et al., 2009; Shanley and Bishop, 2012). Due to this large variability, there are no estimates of the total change in loading on surface waters due to forestry practices. However, there is some evidence of responses in fish concentrations (Garcia and Carignan, 2000) and it has been estimated that 10–25% of the Hg in fish in managed forest landscapes can be attributed to logging (Bishop et al., 2009).

In the pan-tropical regions, approximately 9.5 million km^2 of tropical forest area has been converted to agricultural land use, resulting in a significant increase in water yield (GWSP, 2008). Deforestation as a source of Hg pollution was recognised some time ago (Veiga et al., 1994), particularly in regions like the Amazon where deforestation for mining and agricultural purposes is intensive. A relationship between deforestation and Hg contamination of aquatic systems has been demonstrated in many studies (e.g., Farella et al., 2006; Mainville et al., 2006; Béliveau et al., 2009). Soil erosion and degradation enhanced by deforestation exposes the mineral horizon to the elements thus enhancing and accelerating Hg leaching (Mainville et al., 2006). Agriculture in the Amazon is based on the slash-and-burn principle that enables short-term enrichment of the soil with nutrients, but leads to loss of Hg content, which is leached to rivers, entering the aquatic food chain, and posing a potential health threat to local populations (Farella et al., 2006). Soil Hg loss occurs rapidly after deforestation and is related to the massive cation input resulting from biomass burning (Béliveau et al., 2009). Associated Hg fluxes can be quite significant. It was reported that in addition to Hg use in gold mining activities, deforestation due to human colonisation and the consequent elevated soil erosion was responsible for 200–4600 µg/m^2/y (depending on the thickness of soil) of Hg released to Amazonian rivers (Roulet et al., 1999). According to the most comprehensive forest review by the FAO to date (FAO, 2010), deforestation shows signs of decreasing in several countries but continues at a high rate in others. Around 13 million hectares of forest were converted to other use or lost through natural causes each year in the 2000s compared to 16 million hectares per year in the 1990s. Both Brazil and Indonesia, which had the highest net loss of forest in the 1990s, have significantly reduced their rate of loss, while in Australia, severe drought and forest fires have exacerbated the loss of forest since 2000 (FAO, 2010). The actual Hg loss due to deforestation depends on the loss and thickness of the organic horizon. If ~2000 µg Hg/m^2/y is adopted as an average value globally (Roulet et al., 1999) and considering the area deforested reported for 2010, this would result in ~260 t Hg/y released to local aquatic systems. These releases are especially important as they bring new Hg to ecosystems that would otherwise be retained in soils.

Dam construction

On the global scale, significant amounts of the basin-scale sediment fluxes in regulated basins are potentially trapped in artificial impoundments; in the inventory by Vörösmarty et al. (2003) more than 600 artificial impoundments were categorised as large (> 0.5 km^3 maximum storage capacity) and over 44 000 as smaller. Sediment trapping efficiency varies from basin to basin and locally can exceed 80%. The most heavily regulated drainage basins occur in Europe, followed by North America, Africa, and Australia/Oceania (Vörösmarty et al., 2003). In this way, a significant proportion of the Hg associated with river sediments and transported downstream by rivers is trapped by these impoundments. Even more importantly, these impoundments cause increases in MeHg concentrations (in water, sediment and biota) by creating organic-rich anoxic deposits conducive to Hg methylation (Hines et al., 2000 and references therein). Assuming that 25–30% (or 4–5 Gt) of the total global sediment flux is intercepted by reservoirs (Vörösmarty et al., 2003), and comparing this with the total amount of Hg reaching the oceans (see Section 4.3.2.2.1), then ~400–1400 t of Hg annually is expected to be trapped globally by the reservoirs. However, it should be noted that there is a large uncertainty associated with this estimate, as sediment retention varies spatially as well as the Hg content of the sediment itself.

Offshore exploitation and exploration activities

In addition to offshore oil and gas operations (see Section 4.3.2.1.3 for details), there are various other offshore exploration and exploitation activities that can introduce Hg into marine environments. For example, deep sea mining can cause remobilisation and releases of Hg in/to oceans. The basic deep sea mining operations include picking up polymetallic nodules and separating them from the fine-grained seabed muds that host them, lifting them to the ocean surface; and separating them from the seawater and sediment entrained in the lift operation and transporting them to a metallurgical processing facility (Ponge, 2012). The associated environmental impacts are disruption of the sediments, and the discharges from the mining ships (Markussen, 1994). The former causes mobilisation of Hg trapped in the seabed sediments to the water column, as Hg is naturally associated with many of these minerals and can also produce conditions that favour methylation, while the latter is expected to introduce wastewater enriched with Hg directly to surface waters. The extent of these activities can be seen from Figure 4.5 which shows the global distribution of deep seabed resources. Some other offshore activities that can affect oceans and from which it is reasonable to assume that Hg could be released to seas and oceans are ocean traffic, oil and gas pipelines, and offshore wind power installations (EC, 2012).

In general, Hg can be released to oceans due to its presence or use in specific processes associated with these activities. Moreover, during construction and operation of offshore installations, Hg previously immobilised in bottom sediments can be remobilised and released into the water column. Physical perturbation can cause Hg to be transported to environments that favour the production of MeHg. However, as far as is known, these environmental issues have not yet been addressed and no data exist that would make it possible to quantify Hg releases associated with these activities.

4.4 Inventory results

Among the individual sectors/categories for which there is enough information to provide a reasonable estimate of Hg released to aquatic environments, Hg use in ASGM seems to be by far the most important source of Hg. Total worldwide releases of Hg to both land and water associated with ASGM activities are estimated at over 880 t/y; however, how much of this Hg is later remobilised and enters aquatic systems cannot yet be determined. The global estimate of Hg release to water from other point sources totals 185 t/y. Of that, about half (89 t/y) is attributed to disposal of wastes from Hg-containing products, the rest being associated with non-ferrous metal production (especially gold, copper and zinc ore smelting), releases from

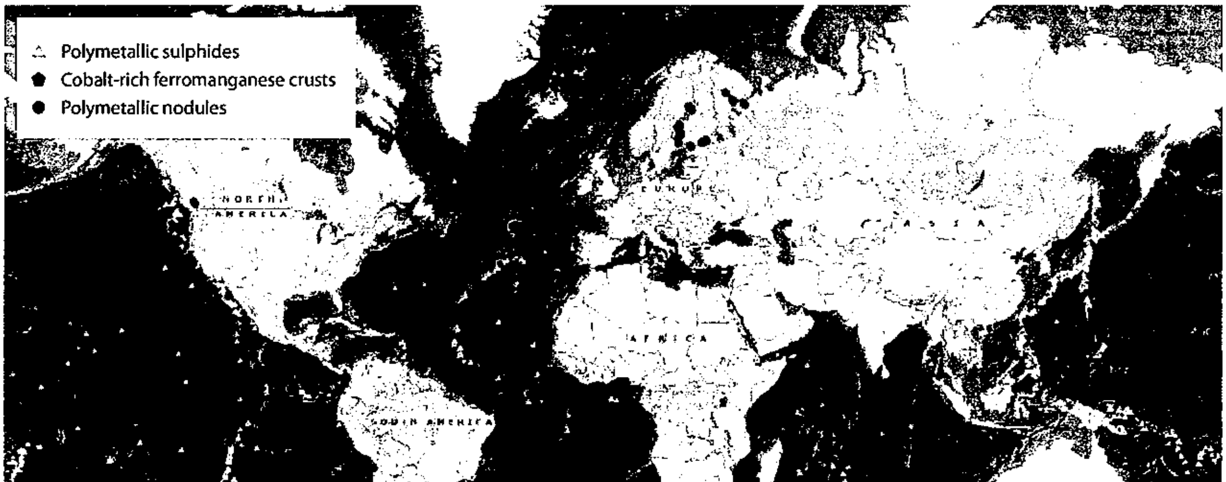

Figure 4.5. Global deep seabed resources. Source: obtained from ISA web GIS application online at: www.mapserver.isa.org.jm/GIS

the chlor-alkali industry and oil refining. In addition to these direct releases, remobilisation of Hg from various contaminated surfaces is estimated to be 8–33 t/y. Deforestation was also recognised as an important source of Hg with 260 t/y released into rivers worldwide. All this Hg released from the various point and diffuse sources enters local aquatic systems and is subjected to riverine transport. On its way to downstream aquatic systems, ~400–1400 t/y is expected to be trapped globally by reservoirs, while ~1200–3700 t of Hg is reaching coastal sites each year. Comparing these values with estimated natural releases from terrestrial environments (150–960 t/y), it is apparent that anthropogenic inputs are a substantial contributor to global Hg releases to rivers, lakes, and oceans.

4.5 Conclusions

4.5.1 Key findings on global releases of mercury to aquatic environments

1. The estimated releases and inputs of Hg to aquatic environments presented here are associated with large uncertainties. Still, the results indicate that anthropogenic sources contribute significantly (thousands of tonnes per year) to the global Hg budget. Based on current knowledge and understanding, it appears that diffuse inputs and direct releases from point sources are equally important.
2. Atmospheric deposition (see Chapter 3 for details) is the most important pathway for Hg to enter both the terrestrial and marine environment. However, in contrast to the oceans, Hg deposited on land is retained in large measure by soils and vegetation, representing a pool for further remobilisation.
3. While export of Hg from non-contaminated catchments does not usually exceed several μg/m²/y, export of Hg from contaminated systems can reach hundreds of μg/m²/y, affecting downstream aquatic systems at distances exceeding hundreds of kilometres.
4. Land management practices such as deforestation and agriculture can lead to enhanced and accelerated Hg leaching from soils, and in this way its entry to aquatic systems. Thus this remobilised Hg from historical natural and anthropogenic sources is introduced into aquatic environments and becomes part of the global cycle. Land management can act as a substantial contributor of Hg to aquatic systems.
5. Higher frequencies and magnitudes of extreme hydro-meteorological events as a result of climate change are very likely to lead to accelerated input of Hg to and transport within aquatic systems.
6. The present estimates of anthropogenic Hg inputs to aquatic environments revealed that due to its current use as well as to Hg historically accumulated in areas where ASGM activities are/were conducted, ASGM can be considered as the major single anthropogenic source of Hg for aquatic systems.
7. There are many other known anthropogenic activities, such as offshore exploitation and exploration, responsible for releases of Hg to aquatic systems, however these are not yet properly addressed in the scientific literature and, to date, there are no independent, openly available data that would make it possible to establish a global quantification of these releases.

4.5.2 Future needs/gaps in information

The estimates presented here have large uncertainties; mostly due to a lack of data in the literature reporting Hg releases to aquatic systems. Extrapolation of releases from site-specific case studies does not take site/sector specific conditions into account. Therefore, in order to reduce the uncertainties the following approach is suggested:

- The mobility and consequent transport of Hg from its source to aquatic environments depend greatly on the chemical form of the Hg that in combination with site-specific environmental conditions (climatic conditions and the topography of the site) determine its reactivity and bioavailability (toxicity). As only limited information is currently available, the generalisations and assumptions stated in this report had to be made for estimating the global releases of Hg to aquatic systems. Obviously, this is an oversimplification of reality that introduces additional uncertainty in the estimates and should therefore be studied in more detail and addressed in future models and scenarios.
- Information regarding global releases of Hg to aquatic systems is still incomplete, also due to the fact that data are not available for some categories that might be important contributors (e.g., landfills, cement production, waste incineration, coal fired power plants etc.). While contributions from these categories are usually considered negligible relative to atmospheric inputs, the number of these sites and installations globally is significant. Releases of Hg to local aquatic systems from such sites may, therefore, also be significant. Similarly, there is a need for more reliable Hg data from offshore exploration and exploitation activities.
- Systematic and harmonised monitoring of Hg releases and inputs to aquatic systems is required, especially in contaminated systems where Hg loads are much harder to predict relative to non-contaminated systems.
- Harmonised approaches for both measurement and reporting of Hg releases from anthropogenic point sources are needed to ensure comparability of data at the global scale.

5. Aquatic Pathways, Transport and Fate

Authors: Peter Outridge, Robert Mason

Contributors: David Kocman, Milena Horvat, John Munthe

5.1 Introduction

Understanding mercury's aquatic pathways and fate is important because naturally-occurring processes within aquatic ecosystems convert the inorganic forms of Hg (Hg0 and HgII), which dominate the airborne and aquatic Hg releases, into the considerably more toxic form, monomethyl mercury (MeHg), which accumulates in marine and freshwater animals. The majority of the human exposure and health risk associated with Hg comes from consumption of marine foods (fish and marine mammals) containing high levels of MeHg (Mahaffey et al., 2004; Booth and Zeller, 2005; Sunderland, 2007; INAC, 2009; AMAP, 2009). Therefore, this chapter concentrates on the pathways and fate of Hg in the world's oceans and its temporal trends in marine food webs. However, freshwater systems in some regions can be important sources of fish for human consumption, especially for subsistence and recreational fisherman and for some indigenous communities. Certain freshwaters (rivers downstream from artisanal gold mining, chlor-alkali facilities, landfills and other point sources of Hg; lakes receiving elevated rates of atmospheric Hg deposition; and reservoirs) may also be significant locations of Hg contamination and subsequent human health risk. Other ecosystems may be especially sensitive even to low-level Hg inputs because of environmental factors such as low pH, high organic matter, large areas of wetlands and regular wet/dry inundation cycles which enhance MeHg formation (Driscoll et al., 2007). Hence, the pathways and fate of Hg in freshwater environments are also described.

5.2 Aquatic pathways and fate

The generalised aquatic pathways of total Hg in the environment, and the sites of MeHg production and decomposition in aquatic ecosystems is portrayed in Figure 5.1. Although the biota and the organic and inorganic composition of freshwater and seawater differ, many of the important processes of the biogeochemical cycle of Hg (such as methylation, demethylation, the dominance of atmospheric deposition inputs, and the importance of organic particle scavenging of Hg to sediments) are common to all aquatic systems (Fitzgerald and Lamborg, 2007). Lakes and rivers, though, are generally more affected by inputs from their catchments, and by sediment processes including MeHg production because the surface area of sediment relative to water volume is large compared to oceans. Generally, inorganic HgII in dissolved or particulate form dominates the total Hg present in most waters (e.g., Mason et al., 1994; Fitzgerald et al., 2007; Jeremiason et al., 2009). Dissolved gaseous elemental Hg (DGM; Hg0) is typically a minor constituent (<30%) of the total Hg pool, and dissolved MeHg (the most toxic and bioaccumulative of the various Hg species) and dimethyl mercury (DMeHg) are similarly often <20% of total Hg. However, both methylated forms combined may be present at concentrations up to 50% of total Hg in some settings (e.g., the Mediterranean Sea [Cossa et al., 2009]; North Pacific Ocean [Sunderland et al., 2009]; Beaufort Sea [Wang et al., 2012b]). In freshwater and many coastal environments, methylation of inorganic Hg mostly occurs in sediments because of the high microbial activity and near-surface anaerobic zones which

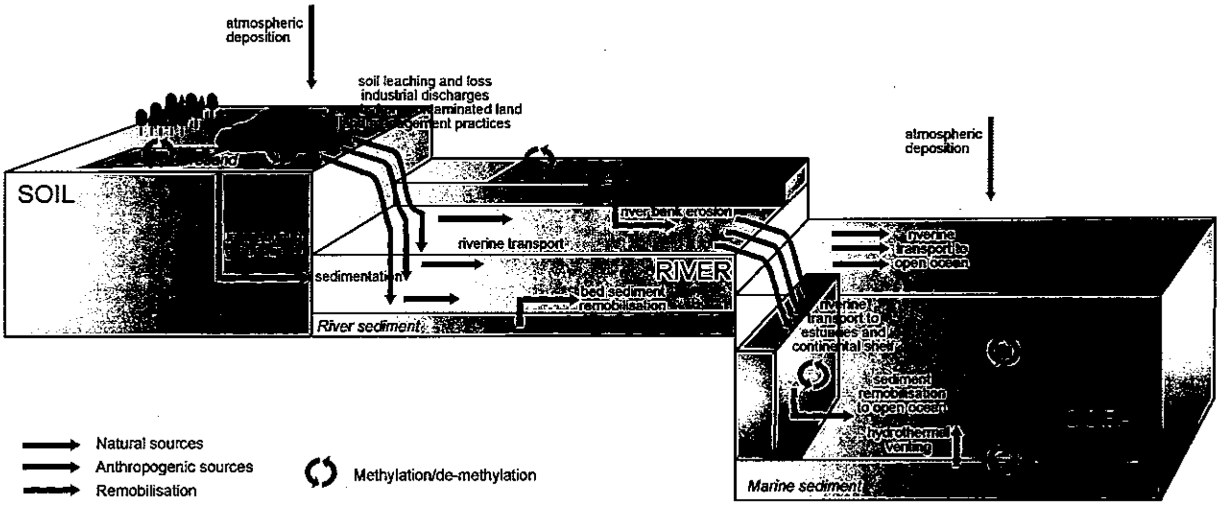

Figure 5.1. Transport pathways of mercury, and general sites of methylation and demethylation, in aquatic systems.

favour sulphate-reducing bacteria. Methylation of inorganic Hg may also occur in anaerobic depths of the water columns of lakes and oceans, but in the ocean methylation occurs to a large degree within the surface to intermediate depths of the water column where anoxia is not known to occur (Fitzgerald and Lamborg, 2007; Sunderland et al., 2009; Lehnherr et al., 2011; Mason et al., 2012). The principal pathways by which Hg is lost from aquatic systems in general are reduction of inorganic HgII to gaseous Hg0 and its volatilisation to air, and burial of particle-associated HgII in sediments (Fitzgerald et al., 2007; Jeremiason et al., 2009; Qureshi et al., 2009). Organic matter (OM) has a high affinity for inorganic Hg and MeHg because of their binding by thiol (SH-) groups present in OM, and therefore dissolved and particulate OM strongly influence the mobility and geochemistry of Hg throughout aquatic ecosystems. In some environments, and particularly in sediments and estuarine waters, binding to inorganic sulphide ligands is also important (Fitzgerald et al., 2007).

5.2.1 The oceans

Model simulations suggest that anthropogenic impacts are generally greatest in the surface mixed layer of the ocean (Soerensen et al., 2010; Strode et al., 2010; Figure 5.2). Throughout this document, the terms 'surface waters' and 'mixed layer' are used to refer to the top 100 m of the ocean, while 'subsurface' or 'intermediate' waters refer to depths below the mixed layer but above the permanent thermocline, that is, from 100 m to typically <1000 m. In the subsurface waters, penetration of anthropogenic Hg is varied and complicated by the regionally-variable lateral and vertical movement of water masses through upwelling and deep-water formation in different ocean basins, and because of sinking and decomposition of Hg-containing particulate material (Mason and Sheu, 2002; Sunderland and Mason, 2007; Strode et al., 2010). Estimates of anthropogenic Hg enrichment vary among models that have different spatial and temporal resolution and consider different transport processes, and evaluation of these models is constrained by limited measurements. One recent estimate (Streets et al., 2011) which includes the impact of human-related Hg releases during the past 500 years suggests that Hg concentrations in the surface mixed layer have increased by a factor of 2–3 over that time while the deep ocean has increased by about 40%. These values are greater than those shown in Figure 5.2, where the increases are estimated for only the past 100 years. Overall, anthropogenic Hg enrichment of deep ocean water is

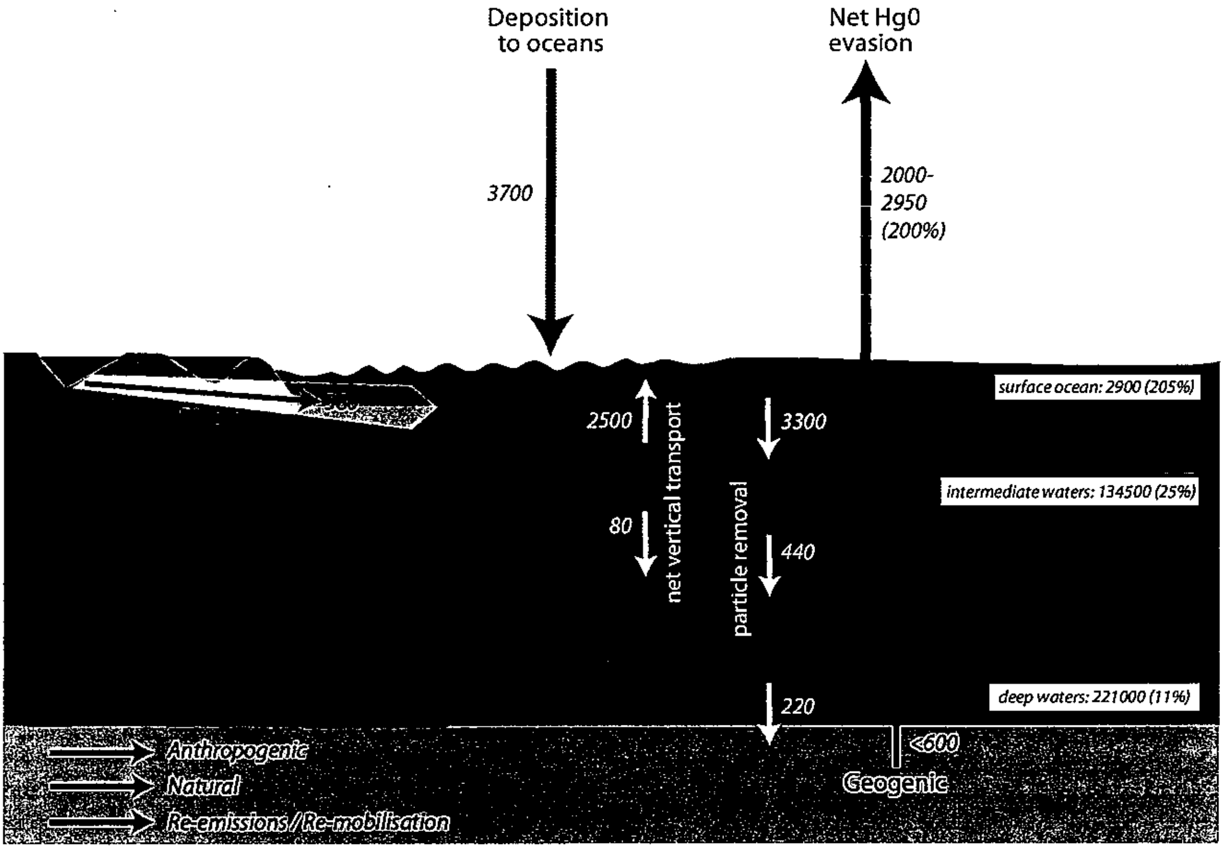

Figure 5.2. A recent estimate of the inventories and fluxes of mercury into and within various layers of the Earth's oceans. Source: adapted from Mason et al. (2012); original Mmol units converted to tonnes by a factor of 200.6. Inventories are in tonnes, and fluxes in tonnes per year. The model is based on simulations using the GEOS-Chem global model, and building on previous studies (Sunderland and Mason, 2007; Selin et al., 2008; Holmes et al., 2010; Smith-Downey et al., 2010; Soerensen et al., 2010). Inventories in different ocean depths shown in square boxes (surface oceans: 0–100 m depth; intermediate waters: 100–1000 m; deep waters below 1000 m depth). The percentage values in brackets are the estimated increases in seawater inventories in the past 100 years due to anthropogenic activities.

much smaller than surface and subsurface waters due to the long time-scales for lateral and vertical transport to the deep ocean (Sunderland and Mason, 2007), which has an overall mixing time of ~1000 years. Understanding the impacts of human activities on MeHg concentrations in marine fish, marine mammals and other marine foods, requires combining knowledge of the time-scales necessary for penetration of anthropogenic Hg in the vertical marine water column with identification of the dominant regions where inorganic Hg is converted to MeHg.

5.2.1.1 Marine inorganic mercury pathways and fate

Sources of Hg to oceans include inputs from ocean margins (rivers, estuaries), groundwater, diffusion from benthic sediments, undersea hydrothermal vents, and direct atmospheric deposition. Except for hydrothermal vents, all of these inputs comprise mixtures of Hg from anthropogenic, natural and re-emitted/re-mobilised sources (see Chapter 4 for detailed discussion of releases to aquatic systems). The most recent modelling effort suggests that total wet and dry deposition to global oceans as a whole in 2008 was 3700 tonnes (Figure 5.2; Mason et al., 2012).

Models and measurements concur that direct atmospheric deposition is the dominant pathway of Hg entry (>80% of total assuming hydrothermal vents contribute 300 t/y; Figure 5.2) (Mason and Sheu, 2002; Dastoor and Larocque, 2004; Selin et al., 2007, 2008; Strode et al., 2007; Sunderland and Mason, 2007; Holmes et al., 2010b; Soerensen et al., 2010; Mason et al., 2012). Exceptions to this general pattern occur in smaller semi-enclosed basins such as the Mediterranean Sea (Rajar et al., 2007) and the Arctic Ocean (Outridge et al., 2008), in which contributions from rivers, coastal erosion or seawater exchange reduce the atmospheric contribution to about 50% of total inputs.

Other Hg pathways to oceans are much smaller on a global basis. Using available discharge and sediment load data on the world's largest 927 rivers (Ludwig et al., 1996; Dai and Trenberth, 2002), Sunderland and Mason (2007) showed that the total Hg load from rivers to estuaries is large (>2800 t/y) but that only a small portion of this Hg is transported offshore (~ 380 t/y, range 240–480), with the remainder trapped by particle settling to estuarine sediments. Riverine inputs can be regionally important. For example, on a basin-wide scale, Hg inputs from rivers ranged from 25% to >50% of the inputs from atmospheric deposition in the South Atlantic Ocean, North Pacific Ocean, and Mediterranean Sea. Conversely they comprise a negligible fraction of inputs in the Arctic, North Atlantic, South Pacific and Indian Oceans (Rajar et al., 2007; Sunderland and Mason, 2007; Outridge et al., 2008).

Limited studies suggest that groundwater Hg inputs and benthic sediment fluxes provide relatively small additions of Hg to the global oceans (~100–800 t/y). Groundwater Hg fluxes into global oceans were derived by assuming groundwater inputs make up ~10% of surface flow (Cossa et al., 1996; Laurier and Mason, 2007; Mason et al., 2012). However, these sources may be regionally significant in some semi-enclosed seas, estuaries and coastal bays with high groundwater outflows, and in seas over active tectonic areas or with a high proportion of continental shelves (e.g., the Mediterranean Sea; Rajar et al., 2007). Dissolved gaseous Hg concentrations exceeding 100 pg/L have been found in extensive areas of deeper water of the Mediterranean Sea, suggesting a benthic source (Horvat et al., 2003; Kotnik et al., 2007), while the sources and levels of DGM in other oceans are areas of active research.

Inputs of Hg from hydrothermal vents are estimated to be <600 t/y (<20% of atmospheric inputs) on a global basis (Lamborg et al., 2006; Mason et al., 2012). Data from four vent locations representing a wide range of geologies showed very high total Hg concentrations in vent fluids (Lamborg et al., 2006), however, scavenging during precipitation of solids removed Hg from vent fluids once they entered seawater, similarly to iron, manganese and other metals (German and Von Damm, 2004). Local enrichment of Hg in hydrothermal-associated mineral deposits and sediments is further evidence for this removal (e.g., Dekov, 2007). In addition, there is the potential for the release of dissolved inorganic Hg from deep ocean sediments. However, various estimates suggest that these inputs are small (Hollweg et al., 2010; Mason et al., 2012).

Gas exchange at the air-water interface is the major removal process for Hg from oceans (see Figure 5.2; Mason et al., 1994, 2001; Fitzgerald et al., 2007; Sunderland and Mason, 2007; Andersson et al., 2011). On a global basis, most (~70%) of the HgII deposited in marine ecosystems is re-emitted to the atmosphere in gaseous form (elemental Hg0 predominantly, but also some DMeHg; Mason and Sheu, 2002; Soerensen et al., 2010; Corbitt et al., 2011). Net biotic and photochemical reduction of HgII to Hg0 occurs in surface waters, and subsequent evasion of Hg0 reduces the pool of potentially bioavailable HgII that may be converted to MeHg and bioaccumulated by marine organisms. A second effect of this evasion is to reduce the amount of Hg diverted by particle scavenging and vertical transport into intermediate and deep waters, where most of the methylation occurs (Mason et al., 2012), and ultimately into sediments. This gas exchange therefore simultaneously prolongs the lifetime of Hg cycling through the atmosphere and biosphere, and partially mitigates the impact of anthropogenic Hg inputs on marine food webs. The prolonged recycling in the atmosphere–biosphere loop, however, also extends the period of impact of any release of Hg to the atmosphere (Smith-Downey et al., 2010).

Any changes in either the efficiency of net reduction in surface waters or the rate of gas exchange will impact the relative rate of change in surface Hg concentrations as well as in atmospheric Hg concentration. One example is the effect of sea-ice cover in the Arctic Ocean which impedes DGM flux into air so that substantially higher DGM concentrations are found under ice-covered areas (Andersson et al., 2008). Changes in the rate of Hg removal from the surface ocean by particle scavenging, resulting from variations in primary productivity, could also affect the extent of re-emission to the atmosphere. In addition, changes in oxidant levels (such as ozone) of the atmosphere will affect the rate of net oxidation of Hg in the atmosphere and therefore the rate of deposition of Hg to the ocean.

5.2.1.2 Marine methylated mercury pathways and fate

Both MeHg and DMeHg, here collectively referred to as ΣMeHg, are present in seawater at detectable concentrations in every region of the world's oceans (Fitzgerald et al., 2007; St. Louis et al., 2007; Cossa et al., 2011). Figure 5.3 presents a global budget for MeHg in the world's oceans. Possible sources of MeHg include production in coastal and shelf sediments (Hammerschmidt and Fitzgerald, 2004, 2006a,b), emissions from hydrothermal vents and remobilisation from deep-sea sediments (Kraepiel et al., 2003), and *in situ* water column methylation and DMeHg decomposition processes (Mason and Fitzgerald, 1990; Sunderland et al., 2009; Heimburger et al., 2010; Cossa et al., 2011; Lehnherr et al., 2011). Evidence strongly suggests that DMeHg is mostly formed by microbial activity during *in situ* water column processes involving inorganic Hg (Fitzgerald et al., 2007).

Atmospheric inputs are likely to be a small fraction of total MeHg supply to the marine environment, ranging from 14–30 t/y (average 20 t/y), assuming that MeHg is 0.5% of total Hg in deposition (Mason et al., 1997; Sunderland and Mason, 2007; Sunderland et al., 2010; Figure 5.3). Evasion of volatile DMeHg to the atmosphere is estimated at 2 t/y (Mason and Benoit, 2003). Even though ΣMeHg in some hydrothermal fluids can range up to 100% of total Hg, especially from rock strata rich in organic matter (Lamborg et al., 2006; Crespo-Medina et al., 2009), hydrothermal vents generally contribute <10 t of ΣMeHg annually to the world's oceans (Mason et al., 2012). The transport of riverine MeHg inputs offshore is estimated at 20 t/y, based on 5% of total Hg being MeHg and assuming that 90% of riverine input is trapped by settling particles in estuarine and coastal sediments (Sunderland and Mason, 2007).

Estimates of the inputs of dissolved MeHg from coastal and shelf sediments to the open ocean range from 2–30 t/y (Cossa et al., 1996; Hammerschmidt and Fitzgerald, 2006a; Hollweg et al., 2010). Part of this variation is an artefact of methodology, with many of the lower estimates being based on simple diffusion models and porewater concentration gradients. Studies with benthic flux chambers provided flux values that are up to an order of magnitude higher than the diffusive estimates (e.g., Gill et al., 1999; Choe et al., 2004; Hammerschmidt and Fitzgerald, 2008). Given the estimate by Fitzgerald et al. (2007) that the fraction of MeHg fluxing from sediments is ~8% of the total Hg sediment depositional flux, and using the global Hg deposition flux to shelf/slope sediments of 580 t/y (Sunderland and Mason, 2007), the MeHg flux from sediments was estimated by Mason et al. (2012) at 42 t/y (see Figure 5.2). However, combining the two approaches suggests that the value may be <40 t/y.

The deposition of MeHg to shelf and slope sediment (~30 t/y, see Figure 5.2), estimated using the fluxes reported by Sunderland and Mason (2007) and 5% MeHg in sedimentary material, is of the same order as the sediment inputs to seawater, suggesting little net transfer overall from coastal sediments to the ocean. Sediment resuspension is a potential source of MeHg in some locations (Kim et al., 2008), and could potentially increase the magnitude of net MeHg flux locally (Benoit et al., 2009; Sunderland et al., 2012). Such data are extremely limited for shelf environments. Relatively high benthic fluxes of MeHg have been estimated for estuarine

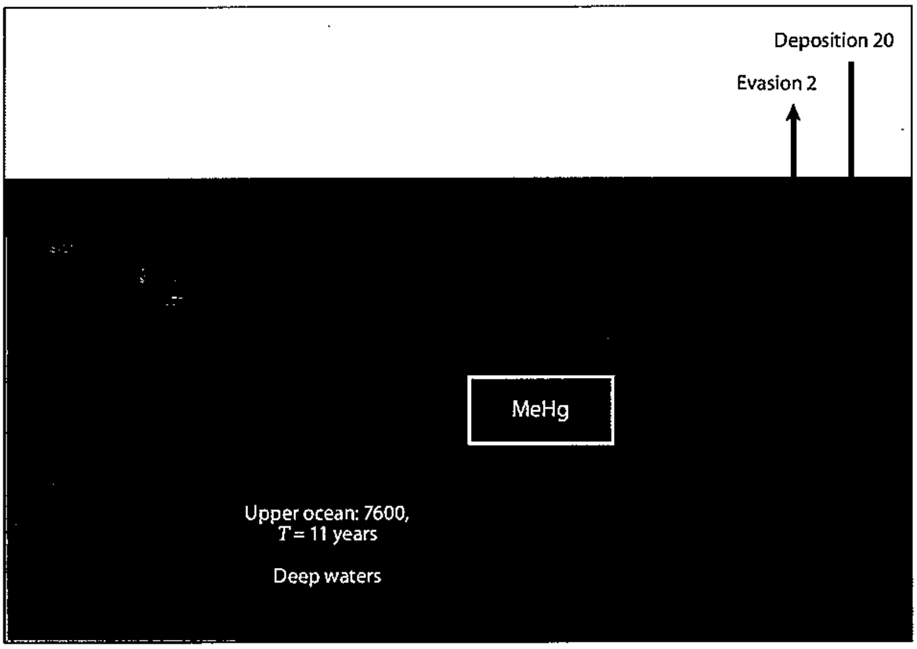

Figure 5.3. Budget for the sources and sinks of monomethyl mercury (MeHg) in the upper ocean (defined as waters above the permanent thermocline, typically <1000 m depth). Source: adapted from Mason et al. (2012). DMeHg – dimethyl mercury. Original Mmol units converted to tonnes by a factor of 200.6. Inventories (in white) are in tonnes, and fluxes (in black) in tonnes per year.

environments such as Baltimore Harbour, Long Island Sound, Chesapeake Bay, San Francisco Bay, and New York Harbour (Choe et al., 2004; Hammerschmidt et al., 2004, 2008; Mason et al., 2006) and for other contaminated environments (e.g., Gulf of Trieste; Covelli et al., 1999), whereas more limited data from shelf and slope sediments confirm that fluxes are lower than in estuaries (Hammerschmidt and Fitzgerald, 2006a; Hollweg et al., 2009, 2010).

The net input to open oceans from coastal environments is likely to vary depending on the extent of the continental shelf and other factors including organic matter and Hg loadings, and hydrologic exchange rates. Sunderland et al. (2010), for example, demonstrated that sediment sources of MeHg were not important in the Bay of Fundy, Canada, and that most MeHg was supplied from external sources (exchange with the North Atlantic Ocean, and river inputs). Similar results can be inferred from mass balance estimates for the inshore coastal sediments of the Gulf of Mexico (Liu et al., 2009), and for the Hudson River estuary, New York (Balcom et al., 2010). However, sediments contributed a much greater fraction in other estuaries, such as Chesapeake Bay and Long Island Sound (Mason et al., 1997; Hammerschmidt and Fitzgerald, 006b).

The flux estimates discussed above indicate that sources of MeHg external to the ocean itself (i.e., riverine inputs, coastal sediments and atmospheric deposition, totalling ~80 t/y) are insufficient to account for the MeHg sinks in the upper oceans (totalling ~380 t/y, see Figure 5.2). These sinks include accumulation into biota and removal by fisheries, photochemical and biological degradation into inorganic Hg, and net removal to deep ocean waters and sediments. This discrepancy suggests that production within the ocean is important. The potential *in situ* sources of MeHg are: production in and diffusion from deep ocean sediments, and production within the water column.

There are few measurements of MeHg in deep ocean sediments and porewater (e.g., Gobeil et al., 1999; Ogrinc et al., 2007; Kading and Andersson, 2011), making estimates of the flux of methylated Hg from these deposits into seawater difficult. Available data indicate very low average concentrations of total Hg in deep ocean sediments, and percentages of MeHg that are equivalent to or less than those in sediments on the continental margins. Studies have estimated for the margins that <8% of the HgII deposited is converted to MeHg and remobilised to overlying water (Fitzgerald et al., 2007). Mercury species concentration data for shelf and slope sediments support these estimates (Hammerschmidt and Fitzgerald, 2006a; Hollweg et al., 2009). This information crudely constrains the global flux of MeHg from deep sea sediments to <16 t/y, which is a minor contribution to the overall budget (Mason et al., 2012).

Pronounced subsurface maxima in both MeHg and DMeHg have been reported from many ocean basins (Kim and Fitzgerald, 1988; Mason and Fitzgerald, 1990, 1991, 1993; Mason et al., 1998; Mason and Sullivan, 1999; Horvat et al., 2003; Kirk et al., 2008; Cossa et al., 2009, 2011; Sunderland et al., 2009, 2011; Heimburger et al., 2010; Bowman et al., 2012; Hammerschmidt and Bowman, 2012). The most conservative explanation for these vertical profiles is the *in situ* formation of MeHg at intermediate depths in association with the natural decomposition of organic matter (Mason and Fitzgerald, 1993; Mason et al., 1998; Mason and Sullivan, 1999; Cossa et al., 2009, 2011; Sunderland et al., 2009). The link to organic carbon degradation is demonstrated by the relationship between MeHg concentrations and the extent of organic carbon remineralisation (Sunderland et al., 2009), by correlations between MeHg and apparent oxygen utilisation (another measure of carbon degradation; Mason and Fitzgerald, 1990, 1993; Mason and Sullivan, 1999; Heimburger et al., 2010; Cossa et al., 2011), and by consideration of Redfield-type ratios between MeHg and phosphate in particulate organic matter in surface and intermediate waters (Cossa et al., 2009).

A recent finding that the kinetic processes producing and degrading MeHg are very rapid within the Arctic Ocean may have significant implications for marine MeHg distribution and bioavailability globally. Lehnherr et al. (2011) used bottle incubations with stable Hg isotopes to demonstrate that methylation and demethylation in Arctic seawater occurred with half-lives measured in days. By contrast, the global mass balance for MeHg suggests an average residence time of 11 years (see Figure 5.3). The explanation for this difference may be that some locations exhibit much more rapid methylation/demethylation kinetics than the global average figures suggest. A logical consequence of this rapid production and destruction is that MeHg transport is laterally and vertically limited in certain environments, such that sharp, local gradients of dissolved MeHg can occur (Lehnherr et al., 2011). Furthermore, the exposure of marine biota to MeHg under highly kinetic systems like this must ultimately be controlled by the capacity for methylation of local inorganic Hg in conjunction with organic matter production and degradation (Wang et al., 2012b).

In addition to direct formation of MeHg from inorganic HgII, remineralisation of sinking particles and decomposition of DMeHg are also potential sources of MeHg (Mason and Fitzgerald, 1993; Mason and Sullivan, 1999). Present understanding suggests that DMeHg decomposition and inorganic Hg methylation contribute roughly equal amounts of MeHg (160 and 150 t/y, respectively) to the upper ocean MeHg pool (Figure 5.2). If MeHg is also produced in the surface mixed layer (as observed by Lehnherr et al., 2011), the low concentrations there suggest that production is balanced by demethylation (Hammerschmidt and Bowman, 2012), and to a lesser extent by bioaccumulation into food webs. Current evidence suggests that the vertical flux and remineralisation of particulate MeHg into deeper waters contributes little to intermediate water MeHg levels (Cossa et al., 2009). Currently, there is little information and consensus on the regions of maximum production of MeHg, although there is a general agreement that the formation is linked to the decomposition of organic matter. Anaerobic bacteria are the major Hg methylating organisms in coastal and freshwater sediments but it is unclear whether they are important in the marine water column because methylation there appears to be most closely linked to the aerobic metabolism of organic carbon (Sunderland et al., 2009; Heimburger et al., 2010). Alternatively, anoxic micro-environments may possibly be created inside sinking particulate organic matter. The microbial pathway responsible for seawater Hg methylation has yet to be confirmed.

Identifying the important locations, processes and net balance between rates of methylation and demethylation in the world's oceans should be a high research priority because this knowledge could help to explain the spatial, temporal and taxonomic variations of MeHg content in marine food webs. For example, in the northern Adriatic region, net Hg methylation in coastal lagoon sediments was controlled by rapid demethylation and the bioavailability of inorganic Hg which was affected by adsorption and precipitation processes (Hines et al., 2012). On the other hand, methylation in offshore marine sites correlated with sulphate reduction rates (Hines et al., 2006). The estuarine to marine gradient in the northern Adriatic is therefore an example of a dynamic system exhibiting horizontally variable rates of microbial activity and Hg transformations that create 'hotspots' of MeHg accumulation which are controlled differently in each region (Hines et al., 2006).

Demethylation, either photolytically or microbially, is the major removal process for MeHg in the upper ocean, based on reported rates of decomposition (Mason and Sullivan, 1999; Monperrus et al., 2007; Whalin et al., 2007; Lehnherr et al., 2011). Overall, the residence time of MeHg is relatively short (~11 years on average) for the upper ocean based on the fluxes in Figure 5.3. This residence time is comparable to the horizontal mixing times of subsurface waters. Therefore it is unlikely that MeHg formed in coastal environments can be transported sufficiently offshore to be a major source for pelagic ocean ecosystems, especially if the very rapid demethylation rates measured in some marine waters (e.g., Lehnherr et al., 2011) are widely applicable. There is the potential for 'bioadvection' of MeHg due to either feeding of offshore fish in coastal environments, or to migration of biota (Fitzgerald et al., 2007). But such transport is bidirectional through the transport of MeHg in biota into and away from estuaries and rivers (e.g., the spawning migration and death of salmon [Sarica et al., 2004]).

The other important fate pathway for MeHg in seawater is uptake into marine food webs. Although only 40 t/y is estimated to follow this pathway, compared to 240 t/y going into demethylation (see Figure 5.2), it is this fraction which presents health risks to marine wildlife and the human consumers of seafood. In terms of its accumulation in food webs, MeHg is especially problematic compared to the inorganic and gaseous elemental Hg dissolved in seawater, for several reasons. First, dissolved MeHg is accumulated by phytoplankton at the base of food webs several times more efficiently and rapidly than inorganic Hg (Mason et al., 1996). The MeHg bioaccumulation step from water to phytoplankton and other seston can be a factor of 10^4 or greater and represents the largest single increase for MeHg concentrations in aquatic ecosystems (Miles et al., 2001; Baeyens et al., 2003). Second, the absorption of MeHg from the gastro-intestinal tract of animals is significantly more efficient than for inorganic Hg (Berlin, 1986; Scheuhammer, 1987). Third, MeHg is the only Hg form to biomagnify in concentration as it progresses from one trophic level to the next in food webs (Campbell et al., 2005; Fitzgerald et al., 2007). Thus, the fraction of MeHg increases progressively with trophic level, typically reaching over 90% of total Hg in the flesh (muscle) of predatory fish and other high trophic level species such as marine mammals (Morel et al., 1998; Campbell et al., 2005) which are consumed by humans. Biomagnification is a key part of the explanation why some indigenous populations that consume top marine predator species have among the world's highest Hg exposures (and blood Hg levels) (AMAP, 2009). Because the magnitudes of atmospheric and waterborne inputs of Hg often do not exhibit a linear relationship with methylation rates and bioavailability, monitoring of environmental Hg requires a comprehensive, spatially-integrated assessment, including high trophic level organisms such as predatory fish and marine mammals as well as abiotic compartments (Evers et al., 2008).

5.2.2 Freshwater environments

5.2.2.1 Riverine pathways and fate

Riverine fluxes of Hg are the consequence of the presence of Hg in terrestrial compartments and its transport due to the processes of erosion and surface runoff within catchments. Globally, total Hg flux in rivers is predominantly associated with suspended particulate matter derived from catchment soils, vegetation, and weathering of exposed rock (Grigal, 2002; Leitch et al., 2007; Brigham et al., 2009; Schuster et al., 2011). The retention of Hg in terrestrial compartments and its delivery to aquatic ecosystems depend on the characteristics of watersheds, such as their size and topography, watershed-to-surface water ratios, land cover and land use (Munthe et al., 2007). Moreover, these ecosystem-specific variables influence the form of Hg delivered and, consequently, its bioavailability and uptake into aquatic food webs (Munthe et al., 2007). Spatial distribution and levels of Hg within the terrestrial part of the catchments are also important and can vary considerably from site to site, depending on the natural and anthropogenic sources of Hg present, soil organic matter content, and other physiographic features of the catchment. For example, low soil Hg concentrations in boreal and Arctic ecosystems are driven by very low atmospheric deposition rates (Smith-Downey et al., 2010). Geostatistical analysis revealed highly variable concentrations of Hg in European topsoils (from 2 to 100's ng/g) that are directly related to human activities such as agriculture (use of fertilizers, manure and agrochemicals) and correlate with the distance to urban and industrial areas (Lado et al., 2008). Similarly, due to atmospheric loading, mining activities, or urban contamination, contaminated stream systems are found throughout the United States (Scudder et al., 2009). Concentrations of total Hg in bed sediments and water in these streams, as a result of soil leaching and erosion, vary over a wide range from 0.84–4.52 ng/g and from 0.27–446 ng/L, respectively (Scudder et al., 2009).

In a comprehensive review, Grigal (2002) emphasised the influence of catchment characteristics such as vegetation and topography, the size of the catchment (lower flux with increasing catchment size), and the percentage of wetland area as the most important characteristics of the catchment influencing the input and speciation of Hg entering aquatic systems. Annual inputs of Hg reported for catchments of varying sizes are mostly in the range 1–3 μg/m^2/y (Grigal, 2002; and references therein). Similar inputs (0.87–4.36 μg/m^2/y) were reported for eight streams in the USA where atmospheric deposition was the main input pathway of Hg (Brigham et al., 2009). Transport of Hg in these streams was found to be mainly controlled by dissolved organic carbon (DOC) and suspended sediment concentrations in the water column (Brigham et al., 2009). Stream discharge is an important factor as it can be the dominant predictor for Hg flux in freshwater systems (Shanley et al., 2005).

Export of Hg out of catchments contaminated with Hg significantly exceeds export from uncontaminated systems where Hg naturally present in soil and atmospheric deposition are the only sources/pathways. Wang et al. (2004) recognised human induced erosion, urban discharges, materials used in agriculture, mining, and combustion and industrial discharges as the most important sources of Hg contamination in aquatic systems. In addition to various levels of contamination, Hg inputs to aquatic systems from contaminated sites vary greatly, as they depend on the site-specific hydro-meteorological conditions. For example, soil erosion in an area of small scale gold mining activities in the Tapajos River basin in the Brazilian Amazon resulted in the annual export of 1600 kg of Hg (Telmer et al., 2006). In the Thur River basin in France, which is heavily polluted by chlor-alkali industrial activity, the input of Hg is 70 μg/m^2/y, corresponding to 19 kg of Hg exported out of the catchment annually (Hissler and Probst, 2006). Estimated annual Hg fluxes from the Lot River in France, an area affected by coal-fired power plants, mining and metal processing, ranged from 35 to 530 kg/y for the past decade (Schafer et al., 2006).

Hydrology is probably the most important factor influencing the transport of Hg from catchments to downstream environments. It has been shown in many studies that Hg transport is highly episodic, associated with suspended solids during high flow events (e.g., Žagar et al., 2006; Kocman et al., 2011; Riscassi et al., 2011). During these events (storms and flooding), not only is catchment soil erosion enhanced, but river bank erosion and disturbance of bed sediments remobilise previously deposited Hg, which significantly contributes to overall annual loads (Wang et al., 2004). For example, in the Carson River, Nevada, a single major flood event was responsible for the transport of ~1400 kg of Hg which was nearly 87% of the total flux over a 6-year time span (Carroll et al., 2004). During a two month period, over 75% of the total Hg flux in a stream draining an abandoned cinnabar mine site in California occurred in events lasting less than 5 days (Whyte and Kirchner, 2000). In one 200 minute period, the authors recorded 3.4 cm of rain, a 2.6-fold increase in streamflow, and an 82-fold increase in Hg flux (1.2–99 g/min). Similarly, during a large flood that lasted for 8 days, about 4700 kg of Hg was exported out of the Soča River catchment, draining the contaminated Idrija Hg-mine region in Slovenia (Horvat et al., 1999). This amount is approximately three times the annual Hg export from the catchment (1500 kg) under average hydrological conditions (Rajar et al., 2004). In uncontaminated systems, the Hg load in the particulate phase during high-flow conditions can be predicted based on turbidity and Hg concentrations, in conjunction with discharge measurements (Riscassi et al., 2011). Due to the known affinity of Hg with organic matter, especially in forested catchments, concentrations and fluxes of dissolved Hg are strongly related to DOC concentrations and quality (Dittman et al., 2010) which can be then used as a proxy measure to calculate Hg fluxes (Dittman et al., 2009).

Climate change is expected to alter some of the processes described above. For example, it could influence the magnitudes and frequency of flood-related fluxes of Hg, as well as its mobility and bioavailability, which could lead to changes in its uptake and accumulation in aquatic food webs. It is expected that higher frequencies and magnitudes of extreme hydro-meteorological events could increase inputs of Hg to aquatic systems through surface runoff, soil erosion and flooding.

Mercury releases from artisanal and small-scale gold mining (ASGM) are of particular interest in this Technical Report, and so the following section reviews specific knowledge about dispersal and fate of Hg from this activity in rivers. As in other rivers, Hg in rivers downstream from ASGM operations is predominantly associated with suspended particulate matter (Roulet et al., 2001; Telmer et al., 2006; Lacerda et al., 2012). Therefore the distribution and fate of inorganic or liquid elemental Hg released into rivers from ASGM is probably influenced primarily by the mobility, transport and deposition of Hg-containing sediment within the river system.

The Tapajós River, Brazil, one of the major Amazonian tributaries most affected by ASGM since the 1970s, has been relatively well studied compared to other ASGM-affected rivers around the world, and there is some evidence of comparatively high fish MeHg levels in the area of ASGM operations in this river (Berzas Nevado et al., 2010). However, a review of the literature concerning ASGM impacts showed that there remain many basic geochemical knowledge gaps which limit understanding; even the role that ASGM plays as a source of riverine Hg contamination is under debate (Berzas Nevado et al., 2010). Early mass balance studies in the Tapajós and other Amazonian rivers concluded that mining and gold processing was responsible for extreme river and fish Hg contamination (e.g., Pfeiffer et al., 1993). However, the sampling integrity and data quality from these early studies have been questioned (Roulet et al., 2001). More recent studies (Roulet et al., 1999, 2001; Telmer et al., 2006) argued that the dominant cause of high Hg concentrations in Tapajós river water and fish was not directly the loss of Hg from ASGM operations. Instead, the disturbance and re-mobilisation of large quantities of Hg-enriched sediment and floodplain soil during mining was thought to be responsible. Similarly, Lacerda et al. (2012) concluded that the remobilisation of Hg naturally present in forest soils, during conversion of forest to other land uses, and not historic ASGM mining, was responsible for relatively high Hg levels in the Madeira River, western Amazon. Although the Amazon generally is not underlain by mercuriferous rocks, high organic matter detritus from the productive terrestrial vegetation may act as a Hg concentrator and promoter of methylation in the extensive areas of seasonally-inundated floodplain soils (Roulet et al., 2001; Wasserman et al., 2003).

Elsewhere, highly elevated concentrations of Hg in water and sediment have been reported within a few kilometres downstream of ASGM operations in Zimbabwe and Tanzania (van Straaten, 2000). The downstream distribution of this contamination was curtailed within a few kilometres by the presence of swamps, and iron oxyhydroxide-rich lateritic soils, which appeared to trap or adsorb dissolved and particulate Hg. The use of Hg in gold mining operations in several Asian countries has also been found to result in locally-contaminated aquatic ecosystems (Li et al., 2009), however the geographic dispersal of this pollution was not studied. The aquatic fate of Hg released from ASGM operations is therefore presently unclear; site- and ecosystem-specific factors including the form of Hg emitted, topography, drainage patterns, and soil organic matter, among others, may determine the ultimate extent and severity of aquatic ecosystem contamination from ASGM.

5.2.2.2 Lake pathways and fate

Empirical data and modelling studies indicate that there are many similarities in general between the important Hg pathways and fate in lakes and in the ocean, but with obvious differences in scale. Modelling of Hg dynamics in a series of four diverse lakes ranging from the world's largest, Lake Superior, to small lakes with a history of direct Hg inputs, showed that photoreduction of inorganic Hg in water followed by evasion of DGM to air, and burial in sediments, were the dominant inorganic Hg removal mechanisms in all of the lakes (Qureshi et al., 2009). Net demethylation in sediments and water outflow were the main pathways removing MeHg. Atmospheric deposition and water inflow from other lakes and/or from the catchment were the dominant inorganic Hg inputs. These findings are generally corroborated by mass balance studies from a wide range of lakes, except that photodemethylation of MeHg in the upper water column has been shown to be an important loss process in many lakes as it is in the ocean (e.g., Sellers et al., 1996; Fitzgerald et al., 2005; Hammerschmidt et al., 2006; Jeremiason et al., 2009), with the rate dependent on organic content and water transparency. In Lakes Superior and Michigan, there was evidence for net MeHg production in the water column (Qureshi et al., 2009), similar to that reported recently in seawater (see Section 5.2.1.2). However, in general the main source of MeHg in lakes and rivers is diffusion from anoxic sediments including wetlands, where sulphate-reducing bacteria are believed to be primarily responsible (Gilmour et al., 1992; Hammerschmidt et al., 2006).

The influence of atmospheric deposition as a factor in MeHg levels in freshwater biota can be seen in the significant correlations between air-water Hg flux and MeHg levels in fish (Hammerschmidt and Fitzgerald, 2006c) and insects (Hammerschmidt and Fitzgerald, 2005) across broad geographical regions of North America. Such a relationship is also demonstrated by Hg isotope spike studies in mesocosms (Orihel et al., 2006) and in whole lake ecosystems (Harris et al., 2007). However, these findings should not be interpreted to demonstrate the immediate and direct uptake of Hg from atmospheric deposition into biota, because the Hg has to be first transported to the sites of methylation, which in freshwaters are dominantly sediments. The studies noted above may suggest that recently deposited Hg is more labile, but there is much evidence for methylation of *in situ* Hg. For example, there is isotopic evidence that MeHg in freshwater fish comes from the methylation of historically-deposited inorganic Hg in sediments and not directly from that in present-day deposition (Sherman and Blum, 2012). The geographic correlations between deposition and biotic Hg levels described above may therefore represent a first-order approximation reflecting the long-term accumulation of deposited Hg in sediments, its ongoing methylation, and subsequent uptake into lake food webs. When comparing biotic Hg between waterbodies, the varying inputs from watersheds, fringing and upstream wetlands, system dynamics and size, and the number of trophic levels in lake food webs, as well as the differences in net methylation potential driven by biogeochemical factors, are all important in determining the MeHg concentration in freshwater biota (Branfireun et al., 2005; Munthe et al., 2007).

The creation of artificial impoundments and reservoirs has been shown in many cases to rapidly induce significant increases of total Hg and MeHg in water and of MeHg in fish and other aquatic species (Lodenius et al., 1983; Bodaly et al., 1984; Paterson et al., 1998; Thérien and Morrison, 1999). Montgomery et al. (2000) showed that this effect did not occur in neighbouring natural lakes, thereby demonstrating that the effect was linked to reservoir formation. The decomposition of submerged organic matter leading to anoxia in bottom waters, coupled with the microbially-driven methylation of the inorganic Hg present in flooded soils and vegetation, is believed to be the primary mechanism responsible in most instances (Hecky et al., 1991; Thérien and Morrison, 1999). After evaluating the biogeochemical controls on biotic Hg levels in the Three Gorges Dam in China, Wang and Zhang (2012) concluded that a cascading effect on multiple internal ecological, geochemical and physical processes was initiated by impoundment, most of which would lead to long-term increases in biotic Hg.

Downstream effects have also been reported following the release of Hg-contaminated reservoir waters (e.g., Bodaly et al., 1997). In some cases, water and biota Hg levels return to pre-impoundment values after 10 to 30 years (Montgomery et al., 2000; Bodaly et al., 2007). However, many reservoirs have organic-rich or wetland-fringed shorelines which experience wet-dry cycles as a result of regular water level drawdown. These ecosystems, especially those ringed with an extensive shallow littoral zone, are likely to be subject to long-term elevated MeHg concentrations in predatory fish and other high trophic level biota (Evers et al., 2007).

5.3 Anthropogenic impacts on aquatic mercury levels

5.3.1 Increases in seawater mercury

Examining the temporal trends of Hg in aquatic systems can potentially be a more robust and accurate measure of the degree of impact of anthropogenic activities in many cases than geographic comparisons. Spatial assessments of anthropogenic impacts on Hg levels can be confounded in some instances by varying underlying geogenic inputs or by fluctuating anthropogenic inputs in regions close to urban/industrial areas.

However, it is difficult to accurately gauge and interpret temporal change over years and decades in the concentration of Hg in seawater. It is possible to compare profile information collected at the same location and separated by significant periods of time; it is also important to keep in mind caveats about the effects of variability in water mass lateral and vertical transport. For example, as pointed out by Laurier et al. (2004), there can be measurable seasonal changes in Hg in the upper ocean water column concentrations that could be the result of deposition/mixing or alternatively result from changes in currents and ocean properties. Given intra-annual variation at any one site, the prospect of trying to discern and attribute causation to relatively small changes in Hg levels in the mixed layer over a few decades is challenging.

With that qualification in mind, two studies have reported evidence for opposing temporal trends in the Atlantic and Pacific Oceans over recent decades. Results suggest that Hg levels have increased in the North Pacific Ocean between 200 and 1000 m (i.e., below the mixed layer) during the past few decades (Sunderland et al., 2009). Results from near Bermuda in the North Atlantic, on the other hand, suggest that there has been a substantial decrease in Hg concentration and change in the water column Hg profile (Mason and Gill, 2005). Other time-series data from the North Atlantic support this finding (Cossa et al., 1992). Studies on the Mediterranean Sea also indicate a decrease in water Hg concentrations between 1990 and 2004 (Coquery and Cossa, 1995; Cossa et al., 1997, 2009; Kotnik et al., 2007). Atmospheric trend studies from around the North Atlantic margin corroborate the declining trend observed in seawater (see Chapter 3 of this report). The trends in the available data are therefore consistent with the idea that Hg levels in the North Atlantic and Mediterranean were significantly perturbed during the past 30 to 50 years (at least) but are now recovering as industries in North America and Europe have gradually improved emissions control technologies (Pirrone et al., 2010; AMAP, 2011), whereas the North Pacific may be exhibiting Hg increases as a consequence of increasing atmospheric emissions from Asia.

5.3.2 Impacts on mercury in marine food webs

Owing to the inherent difficulties in consistently sampling and accurately interpreting seawater Hg time trends, a complementary approach is to determine the temporal trends of Hg in the tissues of aquatic biota, which integrate seawater Hg variations over relatively long periods of time (from months to decades depending on the type of tissue and species ecology; Outridge, 2005). As the Arctic is relatively remote from major urban/industrial regions of the world, the recent temporal trends of Hg in Arctic biota can indicate whether global background levels of Hg in food webs are changing. In the recent Hg assessment in the Arctic (AMAP, 2011), 83 time-series of Hg in marine, terrestrial and freshwater biota spanning the past two to three decades were statistically analysed. Although almost half of the time-series showed no significant trend, most of the increasing trends were in marine species (Rigét et al., 2011). Most of those occurred in northern Canada and Greenland, despite reductions in North American emissions in recent decades.

Reconstructing the long-term trends of Hg in animals back to pre-pollution times (conventionally set as pre-1800 AD) is a robust method of determining the impact that human activities have had on Hg levels in aquatic biota today. Animal hard tissues, such as teeth, hair, feathers and eggshells are useful long-term archives of biological Hg concentrations, because they tend to preserve well in dry, cold or low-oxygen environments such as polar regions or sedimentary deposits (Outridge, 2005). Also, studies with laboratory and wild animals indicate that Hg concentrations in mammalian hair and teeth, and in bird feathers, are correlated with the animals' intake of organic and inorganic

Hg and with their tissue concentrations of Hg (Born et al., 1991; Eide and Wesenberg, 1993; Eide et al., 1993; Bearhop et al., 2000; Outridge et al., 2000).

A review of the global literature revealed no long-term trend studies with freshwater animals. For marine animals, several studies are available from different regions of the northern hemisphere particularly from the Arctic. But because marine ecosystems are a key link to human Hg exposure via food, changes of Hg levels in marine animals can illuminate how human exposure from these sources may also have changed over the past few centuries. For the Arctic long-term data, hard tissue Hg concentrations from different species were converted to a percentage basis, whereby the highest annual median concentration in recent decades was set to 100%, and the 19th century and pre-industrial median concentrations were calculated as percentages of the recent values (Dietz et al., 2009). This approach was necessary because absolute concentrations in different species varied by three to four orders of magnitude both in the pre- and post-industrial period. Using percentages, the trends could be represented in a consistent and comparable manner across species. A consistent long-term pattern was found across a number of marine species (Figure 5.4). Mercury concentrations between the 13th to 16th centuries were relatively stable but increased on average by over 12-fold during the 20th century. The pre-industrial hard tissues contained on average 7.6% (range 5.6–26%) of the maximum annual average Hg levels in the same species in the same areas during recent decades. This finding means that, on average, 92% (range 74–94%) of the present-day Hg in Arctic marine wildlife is likely to be of anthropogenic origin. A similar finding (96% anthropogenic) was reported by a more recent study using polar bear hair from northwest Greenland (Dietz et al., 2011).

Similar findings to those from the Arctic were reported for a 700 year sequence of seabird eggshells from an island in the South China Sea (Xu et al., 2011). Between 1800 and 2000, eggshell Hg concentrations increased steadily, with a particularly rapid increase after 1970, so that average Hg levels over the past two hundred years (15.1 ng/g, n = 9) were more than four times higher than pre-industrial levels (mean 3.45 ng/g, n = 53). Recent (2008) concentrations were 36.7 ng/g dw (n = 4, range 33.8–41.8 ng/g), about ten times higher than the pre-1800 levels. This is equivalent to an anthropogenic Hg contribution of 91% in modern eggshells, using the Dietz et al. (2009) calculation method. For the Antarctic, a 2000 year record of Hg in seal hairs was retrieved from a lake sediment core (Sun et al., 2006). The Hg concentrations (ca. 1 µg/g) in the pre-industrial period were on average about 60% of those in the uppermost sediment layer (1.7 µg/g), which would suggest an anthropogenic contribution of about 40% of total Hg in modern elephant seal hair. This contribution is less than half of that in marine biota in the Arctic Ocean and South China Sea, and is in accordance with lower anthropogenic Hg emissions and lower atmospheric Hg concentrations in the southern hemisphere compared to the northern hemisphere (see Chapters 2 and 3 of this report).

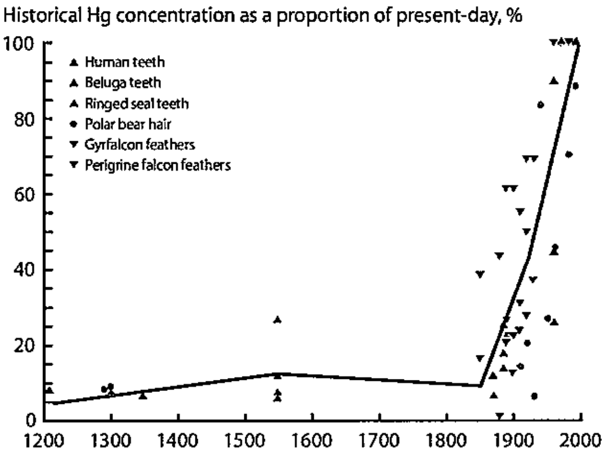

Figure 5.4. Historical trends in mercury concentrations in the hard tissues of Arctic animals and humans, expressed as a percentage of modern maximum annual average concentrations. Source: adapted from AMAP (2011) and Dietz et al. (2009). Most points plotted represent mean values of multiple samples; for beluga and seal teeth, these are presented for different age classes. Original data sources: beluga teeth (Outridge et al., 2002, 2005, 2009); ringed seal teeth (Outridge et al., 2009); human teeth (Eide et al., 1993; Tvinnereim et al., 2000); polar bear hair (Wheatley and Wheatley, 1988; Dietz et al., 2006a); and gyrfalcon and peregrine falcon feathers (Dietz et al., 2006b). Regions covered by these datasets include parts of the Canadian Arctic, Greenland Arctic, and northern Norway).

Museum specimens of seabird feathers were used to demonstrate two-fold MeHg increases since 1880 in black-footed albatross in the North Pacific Ocean (Vo et al., 2011), and three- to six-fold increases since 1885–1900 in shearwaters and petrels in the subtropical North Atlantic (Monteiro and Furness, 1997). These increases are smaller than those from the longer-term datasets from the Arctic and the South China Sea, and may be because the datasets started late in the 19th century after industrialisation had already had an impact on biotic Hg levels.

The above conclusions assume that the long-term increases in Hg concentrations in marine biota occurred solely as a result of increased inputs of Hg from pollution sources, and that potentially confounding factors such as coincident changes in the cryosphere, biogeochemical processes (such as changes in methylation rate or Hg reduction rate), diet, food-web structure or other ecological factors (see AMAP, 2011, Chapters 4 and 5) did not significantly affect the Hg trends. The possible effect of many of these other processes is difficult to assess, first because of a lack of long-term data concerning how these processes have changed in the specific areas in which the long-term Hg studies were conducted, and second because of uncertainty as to how and to what degree these types of change might affect Hg levels in biota. However, by inferring possible dietary behaviour changes using stable isotopes of carbon and nitrogen, several studies (Outridge et al., 2002, 2009; Dietz et al., 2011; Vo et al., 2011) found no evidence that such changes had interfered with interpretation of the temporal Hg trend data (see also Dietz et al., 2009).

5.3.3 Timing of long-term biotic increases

The timing of long-term increases of Hg in biota can be informative about the likely continental sources of the Hg pollution which gave rise to these increases. As no data were available for the Arctic from the period between the 16th century and about 1850, it is not possible to precisely identify the onset of the steep industrial era increase. However, based on the shape of the curve it seems plausible that, on average, Hg in Arctic marine ecosystems started to increase somewhere between 1850 and 1900, with a clear acceleration in the rate of increase after 1900 (see Figure 5.4).

The same conclusions were drawn by individual studies with sufficient time coverage in the late 19th and early 20th centuries. After assessing two adjacent and complementary Arctic datasets, that is, Hg in the teeth of beluga in the Beaufort Sea and of ringed seal in Amundsen Gulf, Canada, Outridge et al. (2009) concluded that Hg levels in marine biota in this region were stable from pre-industrial times up to at least the 1890s, with substantial increases occurring between then and the 1990s. Much of the increase occurred prior to 1960. The feathers of seabirds (guillemot species in the Baltic Sea; shearwaters and petrels in the eastern subtropical North Atlantic) displayed marked Hg increases only after the 1890s (Appelquist et al., 1985; Monteiro and Furness, 1997). In the South China Sea, increases of Hg in seabird eggshells appear to have started about 1825 to 1850, earlier than in the Arctic and North Atlantic Oceans (Xu et al., 2011). But this may be an artefact of the scarcity of pre-1850 samples in the other datasets. Taken together, there is substantial empirical evidence of large anthropogenic increases of Hg in pelagic ocean food webs since at least the late 19th century and possibly as early as the 1820s, which coincide with the rise of industrialisation in Europe and North America, and of recent rapid increases in the South China Sea which coincide with industrialisation in Asia.

5.3.4 The time-lag in aquatic ecosystem response

One important conclusion from the air-ocean modelling work is that, on average, the global oceans are likely to have not yet reached equilibrium with present-day atmospheric Hg levels (Sunderland and Mason, 2007; Selin et al., 2010). This response time-lag is due to several factors. First, the average residence time for Hg in the global upper oceans is significantly longer (20–30 years) than that in the global atmosphere (0.8–2 years), and so removal of Hg added to the oceans takes substantially longer than in the atmosphere (Sunderland and Mason, 2007). Second, the global ocean contains a relatively large mass of natural (geogenic) Hg that has been augmented to varying degrees by anthropogenic inputs (see Figure 5.2). For example, of the ~135 000 t of Hg estimated to be presently in subsurface ocean water, ca. 100 000 t is natural, that is, an equivalent amount was present in the oceans prior to the Industrial Era (Sunderland and Mason, 2007). Thus, changes in atmospheric deposition rates will not proportionately alter seawater Hg levels; responses in seawater Hg will be comparatively more muted and will occur more slowly than the changes in emissions. Finally, vertical transport of Hg from this large subsurface reservoir to surface waters returns a substantial amount of Hg back to the biologically productive mixed layer each year, approximately 2500 t/y (38%) out of the ~6600 t/y added to surface waters by all processes (see Figure 5.2). The consensus view among marine Hg scientists is that this unavoidable time-lag in ocean response to changes in atmospheric Hg means that average Hg concentrations in seawater, and in marine biota, are likely to increase slowly for periods ranging from decades to several centuries, even if there is no further increase in atmospheric Hg levels (Sunderland and Mason, 2007; Selin et al., 2010; Mason et al., 2012).

The effect of future changes in anthropogenic emissions on seawater and marine biota Hg levels is also likely to be partly buffered by the significant amount of historically-deposited Hg which is re-emitted from surface soils and the oceans. As discussed in Chapter 2 of this report, these re-emissions act to maintain atmospheric Hg concentrations at higher levels than current anthropogenic emissions would otherwise dictate. Because atmospheric Hg deposition is the major input pathway for Hg entering the world's oceans, re-emissions to air also play an important role in determining current and future Hg levels in seawater. The effects of growing emissions from Asia and other developing regions on seawater Hg levels therefore will exacerbate the impacts of historical pollution from Europe, Russia and North America which is being continually recycled between air, land and oceans. The impacts of these historical emissions are still being fully realised due to the ocean circulation and biogeochemical processes discussed above.

Regional differences in future seawater and marine biota Hg trends are expected, with the time taken to reach equilibrium with the atmosphere predicted to differ as a result of varying circulation patterns, water residence times, and proximity to regions of industrial activity (Sunderland and Mason, 2007; Selin et al., 2010). For example, the time to steady state of the North Atlantic Ocean above latitude 55° N is estimated at 50–600 years, compared to 500–700 years in the North Pacific and 700–1000 years in surface waters of the Antarctic (Sunderland and Mason, 2007). The response of smaller ocean basins and of surface waters will be naturally faster: the Arctic Ocean is estimated to take only 35 years to fully manifest changes in atmospheric inputs (AMAP, 2011), while the surface Mediterranean responds in 10–50 years and the surface Atlantic in 10–30 years (Sunderland and Mason, 2007).

The response of freshwater ecosystems to changes in atmospheric Hg deposition is thought to be more complex than oceans but may be generally more rapid because of smaller volumes, shorter Hg residence times and more rapid mixing (see Qureshi et al., 2009). However, while increases or decreases in current atmospheric loadings often yield an immediate response in Hg levels in freshwater biota, the timing and magnitude of the response depends on system-specific factors and the form of Hg loaded (Munthe et al., 2007). Generally, lakes, reservoirs and rivers that have catchments and sediments loaded with historically deposited Hg, or that receive a larger fraction of their atmospheric inputs from the hemispheric 'background' (which in turn is influenced by long-range transported GEM), or that have larger catchment to water surface area ratios, are predicted to show more muted and slower responses to emissions reductions than systems with smaller catchment to surface area ratios, or which are more heavily influenced by local sources (Grigal, 2002; Munthe et al., 2007; Knightes et al., 2009; Selin et al., 2010; Wang and Zhang, 2012; Tang et al., 2013). Global re-emissions also impact regional and local freshwater ecosystems through their buffering effect on hemispheric atmospheric Hg levels. Re-emissions of current and historically-deposited anthropogenic Hg, and its global distribution in air, means that even regions which have made substantial cuts in local Hg emissions are likely to continue to receive above-background loadings in deposition until global surface ocean and soil Hg levels return to steady-state conditions under stable atmospheric concentrations, a process which may occur on time-scales of centuries to millennia following substantive emissions reductions (Sunderland and Mason, 2007; Selin et al., 2010; Mason et al., 2012). Present atmospheric deposition rates in most regions of North America, largely reflecting the hemispheric GEM concentrations, are continuing to load the catchments of lakes and rivers with Hg despite recent major reductions in emissions and deposition on this continent (Selin et al., 2010).

Apart from re-emissions to air, historical anthropogenic and natural Hg deposition can impact present freshwater Hg levels through the loading of Hg into catchment soils, so that current Hg deposition and stream fluxes are to some extent disconnected. Munthe and Hultberg (2004) demonstrated that Hg fluxes in stream runoff were independent of current rates of atmospheric wet deposition. After completely covering a stream's catchment with an impermeable roof and thereby reducing contemporary wet inputs to zero, stream export rates of total and MeHg were unchanged over the following ten years. Instead, the ongoing release of historical Hg in catchment soils, probably at rates determined by the mineralisation of soil organic matter, controlled stream Hg flux (Munthe and Hultberg, 2004). Similarly, catchment soil retention and slow release of Hg is believed to explain the delayed declines in fluxes to lake sediments following emissions reductions from nearby point sources (e.g., Nriagu et al., 1998; Outridge et al., 2011). Harris et al. (2007) also demonstrated that Hg isotopes added to a lake's catchment were released to the lake at a very slow rate (<1% per year), probably because of binding to soil organic matter, whereas isotope added to lake water began to be assimilated by the lake food web within a year. They predicted that while rapid declines in fish MeHg levels would follow significant reductions in atmospheric Hg deposition, a complete recovery would be delayed by the gradual export of Hg stored in their catchments. In contrast, a large database on Hg in freshwater fish in 73 Ontario lakes showed no recent declines in fish Hg levels in response to declining atmospheric Hg deposition (Tang et al., 2013).

Storage of historic inorganic Hg in lake sediments can have a similar buffering effect on fish Hg levels. Using variations in Hg stable isotope ratios in precipitation, sediments and fish from lakes affected by emissions from a coal-fired power plant, Sherman and Bum (2012) showed that current deposited Hg was not preferentially accumulated in the fish. Instead, historically-deposited inorganic Hg that had accumulated in lake sediments was the source of fish MeHg. This finding is consistent with the general observation that sediments are the main sources of MeHg in lake waters, and that sediment production of MeHg is often dependent on the inorganic Hg supply (Hammerschmidt et al., 2006; Fitzgerald and Lamborg, 2007). Sherman and Blum (2012) concluded that, depending on a lake's physical and biogeochemical processes, decreased atmospheric loading would not necessarily lead to immediate reductions in fish MeHg, and that full recovery to baseline fish Hg levels might take decades to centuries. Although aquatic biota Hg levels are generally correlated geographically with atmospheric deposition rates (e.g., Hammerschmidt and Fitzgerald, 2005, 2006c), this relationship should not be interpreted as evidence for a rapid response of biotic Hg to future changes in atmospheric deposition. Instead, it is likely to reflect geographical variations in the long-term accumulation of deposited Hg in sediments, its continuing methylation, gradual diffusion into water, and eventual uptake into lake food webs. This process also explains why Harris et al. (2007) found a continuing effect on fish Hg levels for several years after adding an isotope spike to lake waters; the isotope may have been initially carried into the sediments where it was added to other inorganic Hg and eventually methylated, prior to its uptake by the lake food web.

Climate warming has the potential to profoundly alter the Hg cycle in the biosphere (Grimalt et al., 2010; Stern et al., 2012). One consequence may be to further complicate the relationship between emissions reductions and Hg levels in aquatic ecosystems (Outridge et al., 2008; Wang and Zhang, 2012). For example, higher temperatures may increase rates of organic productivity, and rates of bacterial activity, in aquatic ecosystems possibly leading to faster conversion of inorganic Hg to MeHg. Precipitation patterns, rates and timing may change the amounts and timing of Hg delivery. Thawing of frozen northern peatlands may release significant amounts of Hg and organic matter accumulated during the Holocene into adjacent water bodies (Rydberg et al., 2010) and the Arctic Ocean (Outridge et al., 2008) with subsequent effects on the rate of Hg methylation.

5.4 Key findings on aquatic pathways, transport and fate

1. Atmospheric deposition is the major pathway for Hg to enter most aquatic systems, both marine and freshwater. The annual rate of deposition of Hg to oceans and freshwaters has increased about two- to three-fold on average since the Industrial Revolution.
2. Delivery of Hg from terrestrial to freshwater systems is mainly associated with soil erosion and consequent sediment transport, and depends on the characteristics of the catchment, especially its size and topography, land cover, land use, and site-specific hydro-meteorological conditions.
3. In rivers, hydrology is by far the most important factor influencing the transport of Hg from catchments to downstream environments. Most of the annual transport is associated with Hg bound to suspended solids during high flow events (storms and flooding).
4. Natural processes occurring within aquatic ecosystems are responsible for converting the less toxic inorganic and elemental Hg forms emitted from anthropogenic and natural sources into the much more toxic form, MeHg. Methyl mercury accumulates and biomagnifies to relatively high levels in the upper trophic levels of marine and freshwater food webs, thus posing a risk to wildlife and humans.
5. The Hg cycle may be strongly affected by changes to the organic carbon cycle, particularly as it pertains to MeHg production in concert with organic matter mineralisation in oceans and sediments. This effect may interact with climate change, especially in aquatic ecosystems experiencing an increase in organic matter productivity or the restriction of oxygen supply due to increased light, nutrient supply or stratification.
6. Studies of the long-term trends of Hg in high trophic level marine animals (seals, seabirds, polar bear, beluga) show that the current biological Hg concentrations are on average about 12-fold higher than in pre-industrial times (i.e., prior to 1800 AD), even in remote regions such as the Arctic. The timing of the initial Hg increases in marine biota roughly coincided with the acceleration of western industrialisation in the late 19th and early 20th centuries.
7. Because of the slow natural rate of removal of Hg from the ocean, seawater contains a large amount of relatively old natural Hg, which has been augmented to varying degrees by anthropogenic Hg pollution. Surface waters to 100 m depth contain about twice as much Hg as a century ago, whereas intermediate and deep waters have about 10–25% more Hg on average, the difference being due to the delayed transport of surface-deposited Hg into deeper water by slow-moving ocean currents.
8. Seawater Hg concentrations are slow to respond to changes in Hg inputs (both increasing and decreasing) because of the slow rate of vertical and horizontal water exchange in oceans, the high proportion of natural Hg present, and the upwelling of some of the Hg in intermediate waters back to the surface.
9. The time-lag in ocean response to changes in atmospheric Hg means that average Hg concentrations in seawater, and in marine biota, are likely to increase slowly for periods ranging from decades to several centuries, even if there is no further increase in global atmospheric Hg levels.
10. Similarly, even for freshwater ecosystems in regions where reductions in atmospheric Hg concentrations have occurred because of recent emissions controls, the current atmospheric loadings continue to load catchment soils with anthropogenic Hg. This Hg is likely to continue to slowly leach out into lakes and rivers, and into freshwater food webs, over the following centuries to millennia.
11. The effect of emissions reductions on Hg in freshwater biota may vary between different types of lakes and rivers. Some areas, such as small temperate lakes and rivers strongly impacted by regional or local anthropogenic sources, may experience a rapid reduction in upper trophic level Hg concentrations. However, others more influenced by the global atmospheric background, or which have heavy loadings of historical anthropogenic Hg in catchment soils or sediments, are likely to recover over much longer time-frames.
12. Because historical Hg emissions continue to circulate in the world's oceans, further increases in atmospheric emissions in future will have long-term consequences for Hg levels in the world's commercial fisheries, and for Hg exposure among indigenous, subsistence and recreational consumers of marine and freshwater foods.
13. Expanded, standardised and integrated monitoring of Hg levels, particularly in the world's oceans, is essential to improve understanding of the impacts of human activities and future changes in emissions on aquatic Hg levels and the resultant human exposure. Integrated monitoring of the Hg cycle, including methylation/demethylation rates, in water, air, sediments and biota at key global locations is recommended. Monitoring should include ecosystems and food webs that are particularly sensitive to Hg loading, for maximum protection of ecological and human health.