



**UNITED NATIONS  
ENVIRONMENT PROGRAMME**

Chemicals Branch, DTIE



# **The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport**



**Geneva, Switzerland  
December, 2008**

The Governing Council, by its decision 24/3 IV, paragraphs 24 (a) and (b), requested the Executive Director to prepare a report on atmospheric emissions of mercury. UNEP cooperated with the Arctic Council's Arctic Monitoring and Assessment Programme to develop a report responding to this request. The AMAP Secretariat was engaged to coordinate the work process.

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Citation: UNEP Chemicals Branch, 2008. The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport. UNEP-Chemicals, Geneva.

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### **Cover photos**

Top-left: Mercury Thermometer Manufacturing: Without Occupational Safety gear. Source: Toxics Link.

Top middle: Mercury flask found in a gold mining village in the Philippines, originating from Almaden, Spain. Source: Lars Hyllander

Top right: Boy covering face to avoid fumes (ineffective) while burning amalgam to evaporate mercury and produce gold.  
Source: Kevin Telmer

Bottom left: Coal fired power plant. Source: [www.shutterstock.com](http://www.shutterstock.com)

Bottom middle: Workers in a cement factory. Source: [www.shutterstock.com](http://www.shutterstock.com)

Bottom right: Red hot slag from the Norilsk (Russia) nickel foundary, glowing at dusk. Souce: Bryan & Cherry Alexander Photography



# Executive Summary

## Introduction

In 2007, the Governing Council (GC) of the United Nations Environment Programme (UNEP) through its Decision 24/3 requested the Executive Director of UNEP:

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

### *Atmospheric emission*

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

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

Mercury and compounds containing mercury are toxic for humans and for the environment. As a naturally occurring element, mercury has always been present in the environment. Human activity, particularly since the start of the industrial age, has mobilized mercury in addition to that already in circulation naturally. Mercury is easily transported by air and water. In its gaseous elemental form, mercury has a long atmospheric lifetime (6-18 months) which means it can be transported around the globe, hence its characterization as a 'global pollutant'. Atmospheric mercury is deposited in various ways to the ground and water. After deposition, some of the mercury can be transformed, primarily by microbial action, into methylmercury. Methylmercury bio-accumulates and bio-magnifies in food webs, resulting in increased concentrations in organisms higher in the food web. For these reasons, mercury remains

an important subject of global pollution control efforts.

UNEP's 2002 *Global Mercury Assessment* examined the reasons for concern about mercury, its toxicology for humans and the environment, sources and levels of environmental mercury, and the prospects for policy actions. It relied on the best available information at that time, which were primarily data from 1995 and before.

In response to the 2007 UNEP GC request, this report *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* and the related *Technical Background Report to the Global Atmospheric Mercury Assessment* address atmospheric emissions (focusing on anthropogenic emissions), emissions trends, and results from modelling.

The new reports update these components of UNEP's 2002 *Global Mercury Assessment*. Specifically, they provide improved emissions estimates, including estimates for product-related emissions; new information on trends in emissions; scenarios that explore future emissions and the prospects for reductions; and the results of recent research on atmospheric transport, modelling, and deposition of mercury.

The new inventory of anthropogenic emissions represents the most up-to-date, state-of-the-art global inventory of anthropogenic emissions of mercury to the atmosphere currently available. The 2005 inventory incorporates new national reporting. In cases where national data are still lacking, improved estimates of emissions have been prepared based on better information from more countries and more accurate statistics and emission factors. The inclusion of emissions associated with product-use and disposal and artisanal/small-scale gold mining represent further significant improvements over previous inventories.

The Arctic Monitoring and Assessment Programme (AMAP) Secretariat was engaged to coordinate the process of developing the reports. This



arrangement ensured efficient mutual cooperation between the work on the UNEP reports and that on the ongoing AMAP mercury assessment. The reports have been subject to national and expert review. The detailed information that provides the basis for the statements made in this report is presented in the fully-referenced technical background report. The reports have also drawn on the work of the UNEP Global Mercury partnership (Mercury Air Transport and Fate Research partnership area) and AMAP.

## Key Findings

### Sources

Mercury is released from a variety of natural sources, including volcanoes and geothermal activity, wildfires and weathering of rocks and soils, and from various human activities. This report focuses on releases from human activities. Mercury is released to the atmosphere during burning of fossil fuels, processing ores from mining, and several industrial processes including the chlor-alkali industry. It is also found in various commercial and consumer products, and is released when waste containing those products is incinerated. The report also recognizes that mercury that has been deposited from the atmosphere can be repeatedly emitted again in various ways.

### Emissions

Global atmospheric emissions of mercury from human activity in 2005 were estimated to be approximately 1930 (range 1230–2890) tonnes. This number is in the same range as estimates of natural emissions from oceans (400–1300 tonnes per year) plus emissions from land (500–1000 tonnes per year). Re-emissions add a further contribution, with natural emissions plus re-emissions estimated to be around 1800–4800 tonnes per year, depending on the source of information and the estimation method. Although it is not possible to distinguish the anthropogenic and natural com-

ponents of re-emissions, the relative proportions are likely to mirror those of the original emissions. Thus, about half of re-emissions can reasonably be considered anthropogenic.

Burning of fossil fuels (primarily coal) is the largest single source of emissions from human sources, accounting for about 45% of the total anthropogenic emissions. Artisanal/small-scale gold mining was responsible for about 18%, with industrial gold production accounting for an additional 5–6% of global emissions from human activities. Other mining and metal production activities are responsible for about 10% of global anthropogenic releases to the atmosphere. Cement production releases a similar amount. Emissions from waste incineration and product-use sources are more difficult to estimate. These emissions could be considerably higher than the generally conservative estimates of 150 tonnes included in the 1930 tonnes global estimate.

Power plants are the largest single source in most countries with high mercury emissions, although in Brazil, Indonesia, Columbia, and some other countries (in South America, Asia and Africa in particular) artisanal/small-scale gold mining is the largest single source.

Geographically, about two-thirds of global anthropogenic releases of mercury to the atmosphere appear to come from Asian sources, with China as the largest contributor worldwide. The United States of America and India are the second and third largest emitters, but their combined total emissions are only about one-third of China's.

The uncertainties associated with estimates of mercury emissions are largely related to the application of various assumptions that are required to make up for a lack of actual measurement data. The figures for anthropogenic emissions are based on governmental emission data where available, combined with estimates for countries that did not provide such data. Some countries that are

Global anthropogenic emissions to air in 2005 from different regions.

Continent	2005 emission, tonnes	% of 2005 emission	Low-end estimate	High-end estimate
Africa	95	5.0	55	140
Asia	1281	66.5	835	1760
Europe	150	7.8	90	310
North America	153	7.9	90	305
Oceania	39	2.0	25	50
Russia	74	3.9	45	130
South America	133	6.9	80	195
Total	1930	100	1220	2900



major mercury emitters did not provide national emissions reports. Other countries, such as South Africa and Japan, provided updated information and more accurate emissions estimates than were available in the past. Measurements made at major point sources such as power plants are few, but where available they have been used as the basis for some emission estimates. The reliability of industrial activity statistics and other statistics used for the purposes of estimating emissions, and the accuracy of various assumptions about specific practices and technologies as they relate to mercury emissions are additional sources of uncertainty. Despite the uncertainties involved, the 2005 emissions inventory and its underlying data are considered to represent a robust inventory of contemporary global anthropogenic emissions of mercury to air, provide a picture of regional and national patterns and give insight into global trends.

### Temporal Trends in Emissions

In 1990, global anthropogenic mercury releases to the atmosphere from sources associated with incidental pollutant emissions, and the intentional use of mercury in the chlor-alkali industry were estimated at about 1910 tonnes. In 1995, estimated emissions rose to about 2050 tonnes, but fell by 2000 to about 1930 tonnes. The greatest decreases were in Europe, with substantial declines also in North America, reflecting the introduction and wider use of emissions control technologies. Emissions in Asia, South America, Africa and Oceania increased modestly over this period, attributed to economic expansion in some countries, with the largest increases seen in Asia.

Comparison of the earlier global inventories with the new 2005 figures is complicated by changes in methods, assumptions, and the addition of new sectors of activity. Using data for only those sectors included in both the 2000 and 2005 global emissions inventories, estimated total emissions from these sectors fell by about 450 tonnes. Some of this decrease is real, whereas some is likely due to improved quality of information, data and estimates. European emissions continued to decline through 2005. In Asia, increases in emissions from China and India were partly offset by declines in emissions from several other countries including Japan.

Scenarios of future emissions have been prepared to help explore the prospects for reducing mercury emissions and the implications of not

taking any action in this regard. These scenarios suggest that, if current trends in industrial development and resource use were to continue, mercury emissions in key selected sectors (those where mercury is an incidental pollutant and also the chlor-alkali industry) are likely to rise from about 1480 tonnes in 2005 to about 1850 tonnes by 2020. However, if emissions controls currently in place or planned in Europe were to be extended worldwide, mercury emissions from these sectors could drop to about 850 tonnes by 2020. Under a scenario of maximum technologically feasible reduction measures, emissions could drop to about 670 tonnes by 2020. Emissions from product use and artisanal/small-scale gold mining were not included in these scenarios. Projecting figures for these sectors is difficult, and the preliminary estimates produced were considered too speculative to introduce into the current scenario evaluation. However, both of these sectors have the potential for significant reductions in mercury emissions.

### Atmospheric Transport and Processes

Gaseous elemental mercury spreads around the world, with regional atmospheric concentrations varying from 1.1 nanograms per cubic meter in remote locations in the Southern Hemisphere to 4 nanograms per cubic meter in East Asia.

Although better information continues to become available as a result of new research, a more complete understanding of the processes that determine mercury transport in the atmosphere is needed to better connect anthropogenic sources to the eventual deposition of mercury and its uptake into food webs. The chemical reactions that mercury undergoes in the atmosphere and in the surface prior to uptake or re-emission are not understood adequately enough to determine exactly what factors promote or inhibit deposition and re-emission.

### Concentrations and Deposition

Atmospheric mercury reaches biota and humans after it has been deposited onto land or water bodies. Studies of sediments, peat, and ice cores provide a long timeline of mercury deposition. Sediments, for example, typically contain about three times as much mercury today as they did in pre-industrial times.

More recent trends are apparent from measurements conducted by several mercury monitoring networks, primarily in the Northern

Hemisphere. Data from air monitoring networks in Europe and North America show a decrease in wet deposition of mercury in the last decade, due to a decline in local or regional emissions. Measurements of mercury air concentrations at remote sites in North America and in Europe tend to show little change in the long-term average. At such locations the levels reflect global atmospheric background concentrations rather than the effect of local and/or regional emissions. On shorter time-scales, however, mercury concentrations in air at remote sites can vary significantly, a prime example being the strong variation at high latitude sites due to atmospheric mercury depletion events at certain times of the year.

### Modelling

Modelling can extend the information gained through observations of atmospheric mercury at individual monitoring sites by examining

the ways that mercury moves throughout the atmosphere and the environment. Modelling results indicating episodic long-range hemispheric transport of mercury are consistent with observations.

One application of models is to explore the regional and global effects of reducing mercury emissions. For example, mercury deposition in Europe has decreased by nearly half since the 1990s. Modelling studies demonstrate that this is likely the result of emissions reductions within the region itself. Despite similar emissions reductions in North America, however, deposition in the region has not declined as much. Models show that this can be partly explained by the changes in Asian emissions. Future emissions reductions in various major source regions can be expected to reduce deposition both within the source region and, to a lesser extent, in other parts of the world.



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# 1 Introduction

## Mandate

In 2007, the Governing Council (GC) of the United Nations Environment Programme (UNEP) through its Decision 24/3 requested the Executive Director of UNEP:

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

*Atmospheric emission*

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

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

This report and the related *Technical Background Report to the Global Atmospheric Mercury Assessment*<sup>1</sup> address atmospheric emissions and trends and results from modelling, and are the response to the GC request. They provide the best available information at the time of analysis and writing, recognizing that new data are continually available.

The technical report is the basis for the statements made in this report and as such is the single reference for this report. The technical report itself is fully referenced according to standard scientific practice. The Arctic Monitoring and Assessment Programme (AMAP) Secretariat was engaged to coordinate the process of developing both this report and the technical report. This arrangement ensured efficient mutual cooperation between the work on the UNEP report and that on the ongoing AMAP mercury assessment. Both reports have

been subject to national and expert review.

The technical report includes an updated inventory of anthropogenic emissions of mercury to the atmosphere in 2005 that is the result of a co-operation between UNEP and AMAP. This inventory is based on national data submitted by some governments in 2007 and estimates prepared for countries that did not provide data. The reports have also drawn on the work of the UNEP Global Mercury partnership (Mercury Air Transport and Fate Research partnership area) through direct involvement of some experts as co-authors of the *Technical Background Report to the Global Atmospheric Mercury Assessment*, use and citation of the partnership draft report that was made available in mid March 2008 and review comments from one partnership expert. The work was also coordinated with the work of the UN ECE Convention on Long-range Transboundary Air Pollution (LRTAP) on mercury.

## Purpose and Scope

In general, it is important to have the best possible knowledge base when making decisions. With regard to hazardous substances, accurate and reliable information on emissions is essential. Estimates of emissions from various sectors and regions are important in assessing the size and scope of the problem and for developing and prioritizing actions. Emission inventories can be used to monitor progress towards reduction goals and to gauge the effectiveness of actions taken. Identifying pathways of transport are important for determining where emissions are likely to cause impacts and, in reverse, where emissions reductions will lead to reduced deposition. All of these steps require a combination of observations, estimates, and modelling.

The present report provides the most up-to-date information available for the worldwide emission and atmospheric transport of mercury. (Note that substantial amounts of mercury are also released to water, but that is not addressed

<sup>1</sup> [http://www.chem.unep.ch/mercury/Atmospheric\\_Emissions/Atmospheric\\_emissions\\_mercury.htm](http://www.chem.unep.ch/mercury/Atmospheric_Emissions/Atmospheric_emissions_mercury.htm)



here). Since this report is aimed to be a basis for decision making, emphasis is given to man-made emissions. It begins with a short overview of natural and anthropogenic sources of mercury, outlining the main sectors involved (Chapter 2). Human activities are then examined in more detail, presenting quantitative estimates of mercury releases from the various sectors, by geographic region of the world in 2005 (Chapter 3). The third part considers trends in emissions, including scenarios for future emissions to point out anticipated problem areas and prospects (Chapter 4).

Next, the report examines what happens after mercury is released, demonstrating the global scope of the problem (Chapters 5, 6, and 7). It begins with a look at atmospheric pathways of mercury (Chapter 5), followed by a review of mercury concentrations and wet deposition (Chapter 6), and concludes with efforts to model mercury transformation, transport, and deposition (Chapter 7).

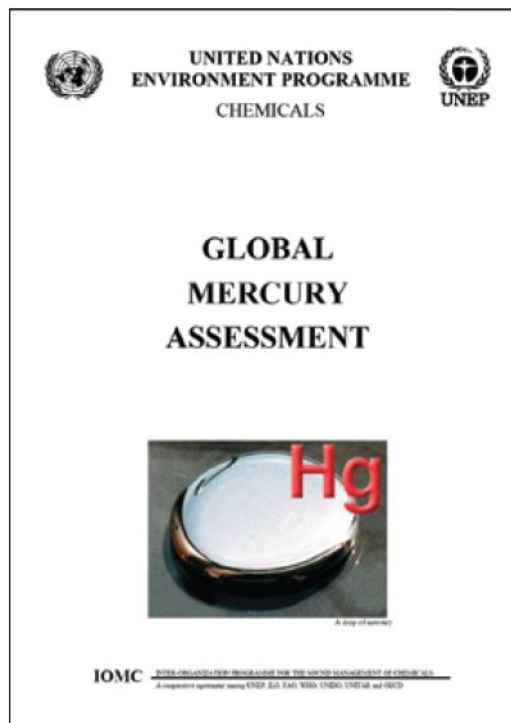
Throughout the report, uncertainties and gaps in knowledge are discussed along with the present state of knowledge. The goal is to present the best available scientific information to help policy makers determine the significance and scale of mercury pollution.

## UNEP's 2002 Global Mercury Assessment

UNEP's 2002 Global Mercury Assessment (GMA) report <sup>2</sup> provided a global overview of the state of knowledge of mercury and mercury compounds. The report includes summary evaluations on a number of scientific and technical topics including: chemistry; toxicology; current exposures and risk evaluations for humans; impacts on the environment; sources and cycling in the global environment; production and use; prevention and control technologies; and data gaps. The GMA also included an overview of initiatives for controlling releases and limiting uses, and a list of options for addressing global adverse impacts. It relied on the best available information at the time. The emissions data were primarily from the 1995 inventory and before.

Mercury and compounds containing mercury are toxic for humans and for the environment. As a naturally occurring element, mercury has always been present in the environment. In its natural state in the earth's crust, however, mercury is usually bound in mineral and other forms. When released to the atmosphere, on the other hand, mercury is usually in its elemental state. Mercury is released to the air, water, and land from various natural and human-generated sources. Once released, mercury persists in the environment where it circulates between air, water, sediments, soil and biota in various forms. It is easily transported by air and water. Atmospheric mercury is deposited in various ways to the ground and water. After deposition, the mercury can be transformed, primarily by microbial action, into methylmercury. In the food web, methylmercury bio-accumulates and bio-magnifies, resulting in increased concentrations in organisms higher in the food web. Methylmercury levels in some fishes and marine mammals have led to consumption advisories in a number of countries.

The 2002 report also noted that additional scientific information was needed to help develop environmental management strategies for mercury, and to improve risk assessment and risk management. Among the knowledge gaps that were highlighted were inventories of national use and releases of mercury and better information on the atmospheric transport, transformation, cycling, and fate of mercury in the environment. The present report addresses these topics, with new information that has been generated since the 2002 report was produced.



<sup>2</sup> <http://www.chem.unep.ch/MERCURY/Report/Final%20Assessment%20report.htm>



## What is new in 2008

The global inventories in the present report are for the year 2005. They have been updated since the 2002 UNEP report and also since the last publication on global inventories (for the year 2000), using new data and better methods for estimating releases. Emissions from major point source categories such as coal combustion have been updated with revised emissions factors and other improved data. For a number of countries emission estimates have been revised or supported using national emission reports and statistics on energy consumption, coal use, and mercury concentrations in various types of coal. In addition, new important emission categories have been added to the global inventory such as artisanal/small-scale gold mining, use of mercury in products (including disposal of waste), and cremations.

Emission inventories are also essential inputs to models of atmospheric transport and deposition, the second topic addressed in this report. In addition to using better data, the models are being continually improved to incorporate advances in understanding of the physics and chemistry of mercury transport, transformation, and deposition. While there are still many areas of uncertainty, current results and understanding nonetheless provide valuable information for policy makers considering various responses to mercury pollution.

Three scenarios for global mercury emissions in the year 2020 have been developed and the results are reported here. Modelling has also been improved by better data, especially concerning the spatial distribution of national emissions data and estimates as well as the improved emissions inventory.

## Types of mercury

Mercury is a metal that is liquid at room temperature. It is most commonly found as the mineral cinnabar ( $\text{HgS}$ ). In the atmosphere mercury is mostly found as elemental mercury ( $\text{Hg}_0$ ), but lesser amounts of mercury are also found in oxidized form either in the gas phase or associated with particles. The individual oxidized compounds are at the moment unknown.

When mercury combines with carbon, it can form a vast number of compounds. All mercury compounds that contain a carbon-mercury bond are classified as 'organic', and can range from simple molecules to large, complex structures. Organic mercury is most commonly found as methylmercury. Methylmercury is produced by bacteria and other microbes and also by abiotic processes. It is of concern because it can bio-accumulate and bio-magnify in the food web. Fish and marine mammals in particular can have mercury levels thousands of times higher than the surrounding water. Although it is only a small fraction of mercury in the environment, methylmercury normally accounts for at least 90% of the mercury in fish. Most human exposure is from consumption of fish, shellfish, and marine mammals.





## 2 Sources of atmospheric mercury

Mercury is a naturally occurring element and is found throughout the world. There are many natural sources of mercury, creating background environmental levels that have been present since long before humans appeared. Mercury is contained in many minerals, especially cinnabar, which is mined to produce mercury. Mercury is a trace element in many other economically valuable minerals and in coal. Human activity, particularly mining and the burning of coal, has increased the mobilization of mercury into the environment, raising the amounts in the atmosphere, soils, and fresh waters and oceans.

Oceans and soils are the major environmental “reservoirs” of mercury. Exchange between oceans, soils and the atmosphere will eventually result in a steady state situation between the levels in these environmental compartments. Reaching such a steady state situation may take years, decades, or even centuries depending on the compartment in question. Mercury levels in the deep ocean, for example, are still rising in response to changes in anthropogenic emissions during the industrial age. Likewise, a long time may be required for a reduction in mercury emissions to cause an observable decline in mercury levels in marine or freshwater ecosystems. However, in some specific locations (such as the Florida Everglades and some Lakes in Sweden) significant decreases in mercury levels in ecosystems have been observed over a relatively short-time period following measures to reduce emissions.

In analyzing mercury emissions and transport, it is important to distinguish various categories of sources. The 2002 Global Mercury Assessment distinguished four types of emissions, each of which is described here in qualitative terms, with particular emphasis on anthropogenic sources.

### Primary natural sources

Mercury in the earth’s crust can be released in several ways. Natural weathering of mercury-containing rocks is continuous and ubiquitous. Volcanoes

add episodic releases. Geothermal activity can also take mercury from underground and emit it to the atmosphere. A major complication in estimating emissions from natural sources is the difficulty of distinguishing primary emissions from (secondary) re-emissions. The amount of gaseous elemental mercury in the atmosphere is reasonably well known. The pathways by which it got there from geological sources and their relative contributions are not as well understood. Some recent models of the flow of mercury through the environment suggest that primary natural sources account for about one-third to one half of mercury emissions to the atmosphere.

### Primary anthropogenic sources

The main primary anthropogenic sources of atmospheric mercury are coal burning, mining for various metals, and industrial activities that process ores or produce cement. In most of these activities, mercury is released as a (by-product) pollutant.

Coal burning, and to a lesser extent the use of other fossil fuels, is the largest anthropogenic source of mercury emissions to the atmosphere. Coal does not contain high concentrations of mercury, but the combination of the large volume of coal burned and the fact that a significant portion of the mercury present in coal is released to the atmosphere yield large overall releases from this sector. The mercury content of coal varies widely, making emissions estimates difficult in the absence of actual measurements of specific coals used.

Mining releases mercury, partly through weathering of newly exposed rock but mainly during the processing of ores, which may have high mercury content in addition to the metal of interest. In the mining and processing of mercury, most of the mercury is captured and used, creating secondary anthropogenic sources, discussed below. The relatively small volume of mercury production makes mercury mining a far smaller primary source than other activities.



Another major primary anthropogenic source of mercury emissions to air is cement production, which often entails the burning of coal to heat the materials required to make cement. Both the fuel and, to a lesser extent the raw materials may contain mercury and lead to emissions. The amount of mercury involved varies greatly due to differences in the mercury content of the fuels and the raw materials. The presence of pollution control measures can greatly reduce emissions from individual plants.

## Secondary anthropogenic sources

Once mercury has been produced for human use, it becomes a potential secondary source. Mercury is used in many products, including batteries, paints, switches, electrical and electronic devices, thermometers, blood-pressure gauges, fluorescent and energy-saving lamps, dental amalgam, pesticides, fungicides, medicines, and cosmetics. For most products in which mercury

is used, mercury-free alternatives exist. Consequently, many of these uses of mercury are declining, at least in some regions, as alternative products or processes are adopted. Mercury-containing lamps are a significant exception, as they are becoming increasingly popular as a means of saving energy and thereby reducing carbon emissions. Further reductions can be promoted by regulatory and market driven means.

Once used, many of the products and the mercury they contain are typically disposed of in landfills or incinerators. While mercury in landfills may slowly become re-mobilized to the environment, waste that is incinerated can be a major source of atmospheric mercury. Incinerators with state-of-the-art controls have low emissions. Smaller quantities of mercury are also released in the re-processing of steel by the secondary steel industry. Much of the steel comes from automobiles, which contain devices that use mercury.



Mercury comes from both natural and anthropogenic sources and has many pathways to ecosystems and humans.



Mercury is also used in various industrial processes. Mercury emissions associated with both industrial/large-scale and artisanal/small-scale gold mining are significant in a number of countries. Gold mining is responsible for some primary source emissions from the raw materials used, as described above for mining in general. More importantly, some methods of gold production use mercury to separate gold from ores and alluvial deposits, resulting in substantial secondary releases when emission controls are not present. Artisanal/small-scale gold mining presents a particular challenge because it is typically small-scale, dispersed, and often illegal or unregulated. Furthermore, the miners are typically poor, have few resources to invest in pollution control devices, and perhaps have little awareness of the hazards of mercury despite having experienced neurological and other effects. An estimated 10-15 million people in 55 countries are engaged in artisanal/small-scale gold mining, producing 20-30% of the world's gold, with another 85-90 million persons indirectly dependent upon this activity.

Mercury is used as a catalyst in the production of vinyl chloride monomer (VCM), particularly in China. Information is lacking on the life-cycle of the mercury catalyst, including the final



Mercury is used in artisanal and small-scale gold mining to extract gold from deposits. Measures to prevent releases are often minimal resulting in environmental contamination and direct exposure to mercury in mining communities.

Environmental Mercury Fluxes from Global Mercury Models

	Lamborg et al., 2002	Mason and Sheu, 2002	Selin et al., 2007	Mason, 2008	Friedl et al., 2008
<b>Hg Fluxes (kt/yr)</b>					
Natural emissions from land	1.0	0.81	0.5		
Re-emissions from land		0.79	1.5		
<b>Emissions from biomass burning</b>					0.675
<b>(A) Total emissions from land</b>	1.0	1.6	2.0	1.85 <sup>a</sup>	
Natural emissions from ocean	0.4	1.3	0.4		
Re-emissions from ocean	0.4	1.3	2.4		
<b>(B) Total oceanic emissions</b>	0.8	2.6	2.8	2.6	
<b>(C) Primary anthropogenic emissions</b>	2.6	2.4	2.2		
<b>Total emissions (A+B+C)</b>	<b>4.4</b>	<b>6.6</b>	<b>7.0</b>		
<b>(D) Deposition to land</b>	2.2	3.52			
<b>(E) Deposition to ocean</b>	2.0	3.08			
<b>Total deposition (D+E)</b>	<b>4.2</b>	<b>6.6</b>	<b>7.0</b>	<b>6.4</b>	
Net load to land	1.2	1.72			
Net load to ocean (burial in sediments)	1.2 (0.4)	0.68 (0.2)			
<b>Total net load (land+ocean)</b>	<b>2.4</b>	<b>2.4</b>	<b>2.2</b>		
<b>Other parameters</b>					
Mercury burden in the troposphere (kt)	5.22	5.00	5.36		
GEM lifetime (yr)	1.3	0.76	0.79		

<sup>a</sup>Including Hg<sup>0</sup> emissions (0.2 kt/yr) in response to Atmospheric Mercury Depletion Events (AMDEs) in polar regions. Biomass burning is not included in the emissions from land in this Table. For table references see the technical background report.



Forest fires re-mobilize mercury. Plants take up mercury from the soil or intercept mercury deposited from the air.

disposal of the mercury. Another major secondary industrial source is the production of chlorine and caustic soda (the chlor-alkali industry) at facilities that use mercury-cell technology. This process uses mercury as a catalyst to produce the chlorine and alkali from salt water. The chlorine is used in the plastics and chemical industries and also for water treatment. The alkali, most commonly sodium hydroxide or caustic soda, is used in commercial and industrial cleaning products. The mercury can be released at several stages in the process. Its use is becoming less common as other processes are adopted, though many plants still rely on mercury-cell technology.

Mercury that is left over from the closure or conversion of mercury-cell chlor-alkali facilities, can be re-sold as a commodity or stockpiled.

## Re-mobilization and re-emission

In addition to emissions from various sources, mercury can also be re-mobilized and re-emitted to the air. Re-mobilization occurs when mercury that had been taken out of atmospheric circulation is released again. For example, mercury accumulated in soils or sediments may be re-mobilized by rain or floods to enter the aquatic system. Mercury taken up by vegetation can be re-emitted to the atmosphere during forest fires or biomass burning. Re-emission occurs when mercury that has been deposited from the air to the surface enters the air once again. Although it is not possible to distinguish the anthropogenic and natural components

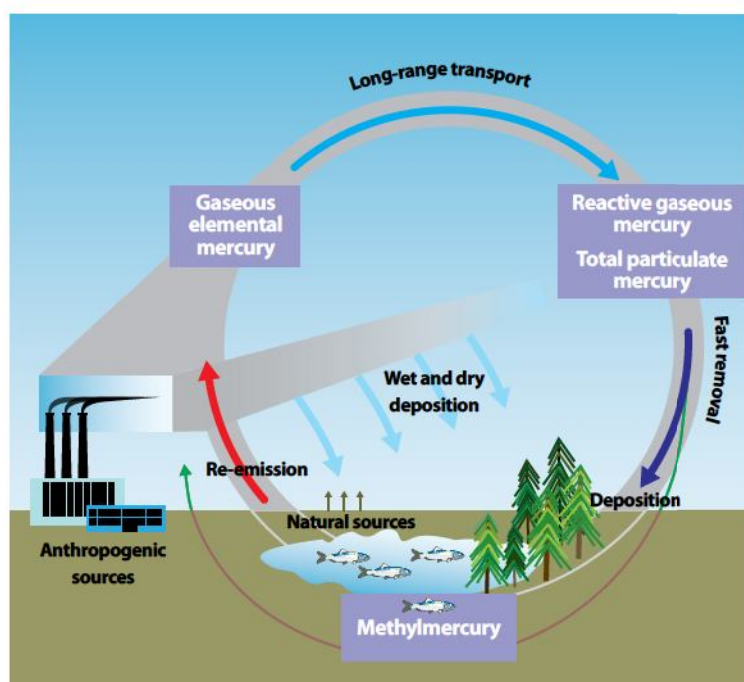
Mercury is transported throughout the world, undergoing chemical reactions, deposition, and re-emission as it cycles through the environment and into food webs.



Canadian Forest Service

of re-emissions, the relative proportions are likely to mirror those of the original emissions. Thus, about half of re-emissions can reasonably be considered anthropogenic (see table on previous page). Re-emission is a common process, for example resulting from the conversion of reactive forms of mercury to elemental mercury, which is likely to return to the air in gaseous form. Mercury may be deposited and re-emitted many times as it circulates in the atmosphere.

Estimating re-mobilization and re-emission is extremely difficult. As is the case with natural sources, re-emission rates must be estimated based on data on atmospheric levels and other observations, in order to balance the amount of mercury in circulation at any given time. Determining re-emission rates also require calculating the respective contributions of various processes, with different chemical pathways, both within the atmosphere and after deposition. Temperature is a key factor. With lower temperatures, re-emission rates are generally lower, potentially leading to higher net deposition in colder regions. In addition, some reactions that remove mercury from the air have been found to occur at higher latitudes due to a combination of circumstances, leading to more rapid deposition in polar regions at certain times of the year. Despite the difficulties in estimating re-mobilization and re-emission, the estimates are crucial for determining geographic patterns of atmospheric transport and deposition.





# 3

## Mercury emissions to the atmosphere

Mercury is released by natural and anthropogenic sources throughout the world. Estimating how much mercury comes from the various sources, by sector and by geographic region, is not simple. For 2005, global anthropogenic mercury emissions to the atmosphere were estimated to be 1930 tonnes. Natural sources are estimated to produce about the same amount of mercury each year. The figure for anthropogenic emissions is based on governmental emission data where available combined with estimates for countries that did not compile such data. These estimates were developed using data on emissions from various human activities and information from various studies carried out in some countries. National data were compared with estimates based on the extent of mercury-releasing activities. The comparison showed that

national reports were consistent with expectations based on the level of industrial and other activities, increasing confidence in the data used. In general, national data have been given priority over general estimates based on the expectation that national experts have greater awareness of local conditions and data, such as production methods and the extent to which pollution control measures are used.

In comparison with the very large number of individual sources, there are a limited number of direct measurements of emissions. Most of the available information is a result of targeted research into emissions from specific types of (point) sources, which can be used to verify some emissions data. Where direct emission measurements are lacking, researchers use a number of assumptions,

Sources of quantitative data used in the preparation and geospatial distribution of the 2005 global inventory of anthropogenic emissions of mercury to air.

	<b>Nationally reported emissions data for 2005</b>	<b>National responses concerning use of mercury in products and mercury in waste<sup>1</sup></b>	<b>National response concerning emissions from, and locations of major point sources<sup>1</sup></b>
General	For all countries <u>other</u> than those listed below, by-product emissions were estimated.	For <u>all</u> countries, emissions from product use (including cremations), and ASGM activities were estimated.	
Africa	Burkina Faso, South Africa		Ghana <sup>7</sup> , Togo <sup>7</sup>
Asia	Cambodia <sup>2</sup> , Japan, Philippines <sup>2</sup> , Republic of Korea	Japan, Nepal <sup>7</sup>	
Europe	All countries <sup>3</sup> , EU25 <sup>4</sup>	Belgium <sup>7</sup> , Denmark, Latvia <sup>7</sup> , United Kingdom	Bulgaria, Croatia, Czech Republic, Finland, France, Germany, Moldova, Netherlands <sup>7</sup> , Norway, Romania, Slovakia, Sweden, Switzerland, United Kingdom, EU25 <sup>4</sup>
North America	Canada <sup>5</sup> , USA (2002) <sup>6</sup>		Canada <sup>5</sup> , Dominican Republic <sup>7</sup> , USA <sup>6</sup>
Oceania	Australia		
South America	Chile <sup>2</sup> , Peru	Chile <sup>7</sup>	Chile
Russia			Russia <sup>8</sup>

<sup>1</sup> Questionnaire circulated by UNEP in connection with development of this report, <sup>2</sup> National reporting employing UNEP Toolkit, <sup>3</sup> Through reporting to the EMEP database on European emissions, <sup>4</sup> Through the European Pollutant Emission Register (EPER) / European Pollutant Emissions and Transfer Register (E-PRTR), for point sources with emissions > 10 kg/year, <sup>5</sup> Through Canadian National Pollution Release Inventory, for point sources with emissions > 5 kg/year, <sup>6</sup> Through the US EPA National Emissions Inventory (latest data available were for 2002), <sup>7</sup> Partial response, <sup>8</sup> Arctic Council Action Programme (2004)



starting with statistical data for a particular activity (e.g. consumption of raw materials or production estimates for relevant materials) multiplied by emission factors for various sectors (which also reflect technologies in use and other factors). For example, emissions from burning of coal are calculated by multiplying the estimated amount of mercury in a tonne of coal by the tonnes of coal burned in a country or region, and correcting for assumed removal efficiency in the flue gas control system. The emission factors represent an estimate themselves, taking into account the variability in mercury content and release depending on a variety of factors for each type of activity.

## Sectoral analysis

By far the largest sectoral source is the burning of fossil fuels, primarily coal. Electrical power plants are estimated to account for about 25% of global anthropogenic mercury emissions to the atmosphere and industrial and residential heating for another 20%. Most of these mercury emissions come from stationary sources – coal-burning power plants or heating facilities. Mercury emissions from oil burning are lower by a factor of ten or more. There are various ways to reduce atmospheric mercury emissions from coal burning at large facilities. Some plants have pollution control equipment to reduce emissions of other pollutants that also reduce mercury emissions at little or no incremental cost. Electrostatic precipitators and fabric filters are commonly used throughout the world to reduce particle emissions from coal burning plants, and they remove up to 30% of the mercury as well. Fabric filters can remove more than that but they are much less frequently used. When these particle control devices are used in combination with sulfur dioxide and nitrogen oxide control devices, the results vary considerably depending on the coal type, but up to 95% of the mercury can be captured with some coals. These combinations of pollution control devices are not found on all plants and are used on only very few plants in the developing world. Mercury control technology for coal-fired power plants capable of capturing up to 95% of the mercury has only recently become commercially available and very few governments require it. Thus currently it is found on only a handful of plants. The use of low-mercury-content coal can achieve also result in substantial reductions in mercury emissions.



➡ Coal burning is the largest single source of anthropogenic mercury emissions to the atmosphere.

Emission factors for Hg used to estimate the 2005 emissions.

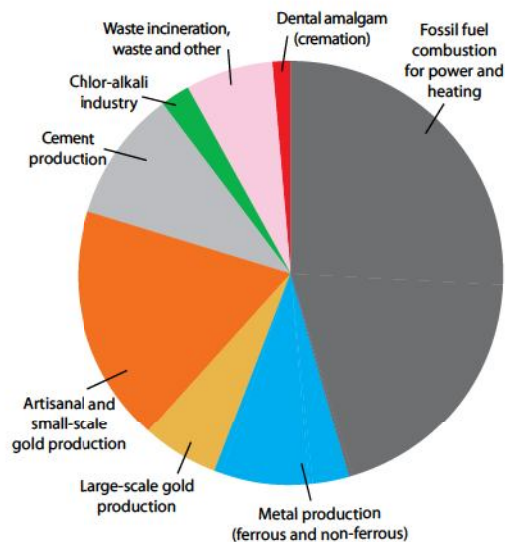
Category	Unit	Emission factor
<b>Coal combustion:</b>		
· Power plants	g/tonne coal	0.1–0.3
· Residential and commercial boilers	g/tonne coal	0.3
<b>Oil combustion</b>	g/tonne oil	0.001
<b>Non-ferrous metal production</b>		
· Cu smelters	g/tonne Cu produced	5.0
· Pb smelters	g/tonne Pb produced	3.0
· Zn smelters	g/tonne Zn produced	7.0
<b>Cement production</b>	g/tonne cement	0.1
<b>Pig iron &amp; steel production</b>	g/tonne steel	0.04
<b>Waste incineration</b>	g/tonne wastes	
· Municipal wastes		1.0
· Sewage sludge wastes		5.0
<b>Mercury Production (Primary)</b>	kg/tonne ore mined	0.2
<b>Gold production (Large-scale)</b>	g/g gold mined	0.025–0.027



Gold production comprises two distinct sources of mercury emissions. First, industrial/large-scale gold production accounts for 6-7% of anthropogenic emissions, from impurities in the gold and raw materials used and in some cases from the use of mercury in processing. Second, mercury is used in artisanal/small-scale gold mining to capture gold by amalgamation with mercury. The mercury-gold amalgam is then heated to remove the mercury, with the result that much of the mercury is released to the atmosphere and into water systems where it can be mobilized and emitted to the atmosphere. The use and release of mercury in artisanal/small-scale gold mining has recently been estimated for the first time. Some 650-1000 tonnes of mercury are released annually, with an estimated 350 tonnes entering the atmosphere directly and the rest released into water systems.

Mining, smelting, and producing metals (not counting gold and mercury itself) account for the third largest sectoral source of mercury emissions, accounting for about 10% of all anthropogenic emissions. The amount of mercury released depends on several factors, including the levels of mercury in the ore or metal, the techniques used in smelting, and the use of pollution control devices. High-temperature roasting and thermal smelting release mercury primarily to the atmosphere, whereas electrolytic extraction is more likely to contaminate water. Today, most major non-ferrous metal smelters use pollution control mechanisms similar to those in power plants, with similar rates of mercury removal. Smaller operations, particularly in the developing world, are unlikely to use any emissions-control technology. The majority of mercury emitted during iron and steel production is from metallurgical coke, a carbon material used in blast furnaces.

Production of cement results in mercury emissions slightly lower than mining and metal pro-



Proportion of global anthropogenic emissions to air in 2005 from different sectors.

duction, contributing an additional 10% or so of anthropogenic emissions.

The use of mercury by the chlor-alkali industry has decreased significantly in the last 15 years as mercury-free methods of production have become more common.

Production of metals is a major source of mercury emissions.



Bryan & Cherry Alexander

Global anthropogenic emissions to air in 2005 from different sectors.

Sector	2005 emission, tonnes	% of 2005 emission	Low-end estimate	High-end estimate
Fossil fuel combustion for power and heating	878	45.6	595	1160
Metal production (ferrous and non-ferrous, excluding gold)	200	10.4	125	275
Large scale gold production	111	5.8	65	155
Artisanal and small-scale gold production	350	18.2	225	475
Cement production	189	9.8	115	265
Chlor-alkali industry	47	2.4	25	65
Waste incineration, waste and other	125	6.5	50	475
Dental amalgam (cremation)	26	1.3	20	30
Total	1930	100	1220	2900



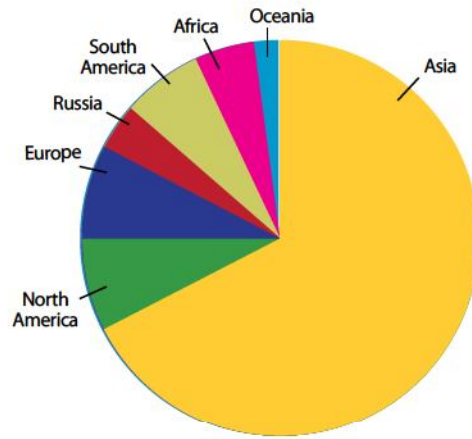
Releases of mercury as a pollutant from mercury mining itself are responsible for less than one percent of anthropogenic emissions worldwide.

In addition to the industrial sectors described already, the disposal of mercury-containing products is another major anthropogenic source, particularly via waste incineration, accounting for 5-7% of total estimated anthropogenic emissions. It is easier to estimate the consumption of mercury in various products than to determine what eventually happens to the mercury. The actual content of mercury in typical waste materials is variable, and waste is handled differently in different places around the world (and even within a single country). Most of the remainder of the waste containing mercury is sent to landfills, with releases to the environment depending on part on the adequacy of the methods used to ensure that the landfill is 'contained'.

Cremation of human remains is estimated, again with considerable uncertainty, to release an additional 26 tonnes of mercury per year from mercury amalgam dental fillings. The use of dental amalgam containing mercury may result in additional releases, for example from the production of the amalgam.

Burning of biomass in wildfires and forest clearing activities have been estimated to yield mercury emissions of around 675 tonnes, making a large contribution to the total emissions. Although accidental wildfires can be considered as a natural source, the mercury released from the burning biomass is partly of anthropogenic origin

Proportion of global anthropogenic emissions to air in 2005 from different regions.



and man-made fires, for example those used for forest clearing in tropical and boreal regions, contribute significantly. Nonetheless, biomass burning is not considered as an anthropogenic source in this report.

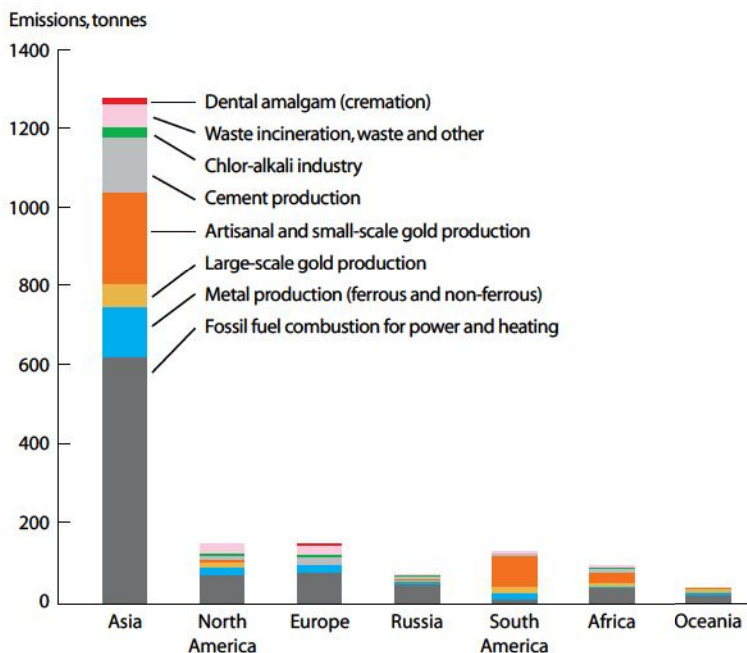
## Geographical analysis

Separating the various sources by continent reveals that, according to the data available for this study, the largest emitting regions in 2005 were Asia, North America and Europe. Asian emissions were more than four times higher than North America and Europe combined. Coal burning accounts for the majority of Asian emissions, with the largest share coming from China. In addition to large power plants, coal burning at the household level is a major contributor to mercury emissions. These small, widely distributed sources are harder to control, often burning low-quality coal mixed with various wastes to meet immediate needs.

According to the 2005 inventory, the three largest mercury emitting countries are China, India, and the United States. On the basis of the information available to this study, the emissions from China are more than double those from India and the United States combined. Together, these three countries release about 57% of global anthropogenic mercury.

The ten countries with the highest emissions levels for mercury have different sectoral patterns of emissions. Power plants and other fossil fuel consumption are major sources in China, India, the U.S., Russia, South Africa, the Republic of Korea, and Australia. In Indonesia, Brazil, and Columbia, by contrast, artisanal/small-scale gold mining is the largest contributor to mercury

Sectoral breakdown by region.





Global anthropogenic emissions to air in 2005 from different regions.

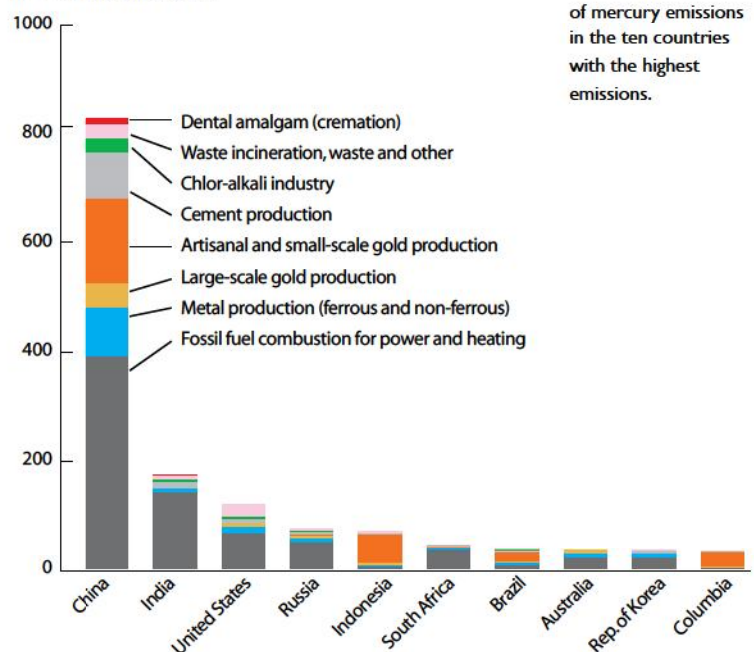
Continent	2005 emission, tonnes	% of 2005 emission	Low-end estimate	High-end estimate
Africa	95	5.0	55	140
Asia	1281	66.5	835	1760
Europe	150	7.8	90	310
North America	153	7.9	90	305
Oceania	39	2.0	25	50
Russia	74	3.9	45	130
South America	133	6.9	80	195
Total	1930	100	1220	2900

emissions. Other differences reflect the relative importance of various sectors to national economies, as well as the degree to which pollution control technologies are in place.

## Uncertainties in emissions

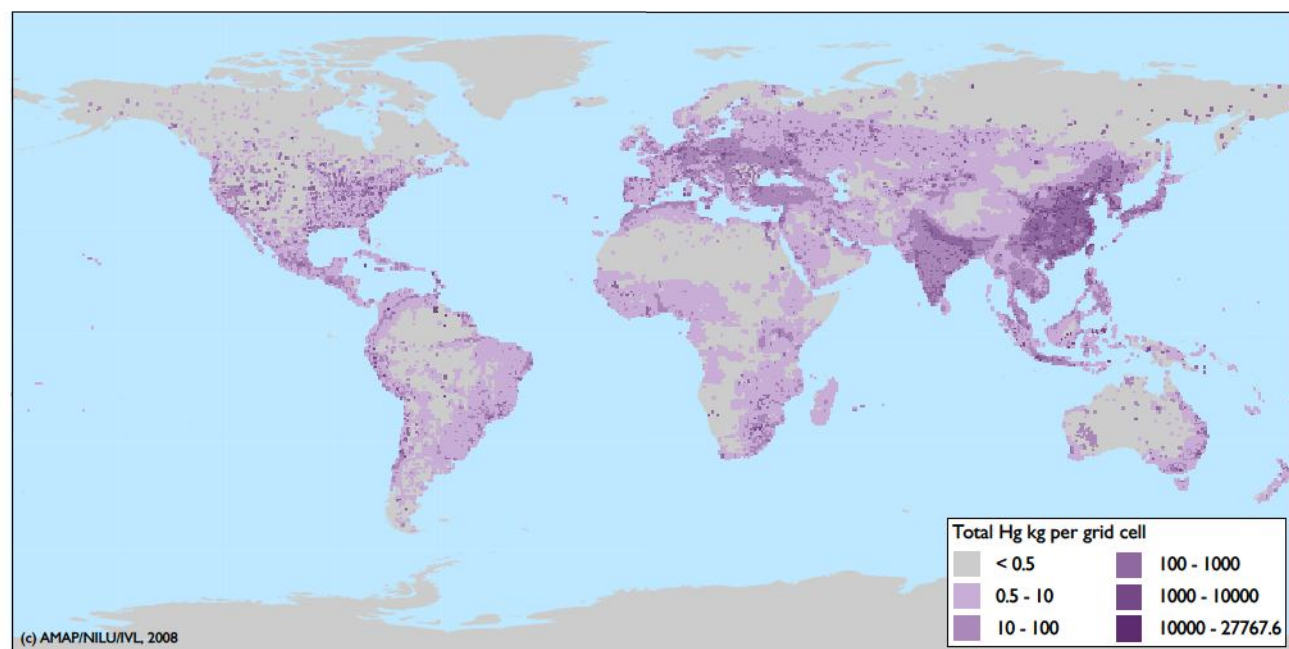
As noted earlier, estimates of mercury emissions are uncertain. The best-studied sources are large, stationary ones such as power plants, but in general few measurements are available. Nonetheless, it is not possible to study each power plant, and so the results from the studies that have been done at some specific facilities are used to estimate releases elsewhere. For other sectors, the estimates have a larger range of uncertainty. Waste disposal and incineration, for example, involve many variables and regional differences. It is important to note, however, that the larger sources have lower uncertainty. Emissions from products containing mercury including dental amalgam are highly uncertain due to uncertainties in both the product life cycles and emission factors. Whether cement production is a greater source of mercury than

Mercury emissions, tonnes



■ Sectoral breakdown of mercury emissions in the ten countries with the highest emissions.

■ Global distribution of anthropogenic mercury emissions to air in 2005. See also the discussion in box on next page.



metal production may not be certain, but the approximate proportion of their contribution to global emissions is likely to be accurate.

Additional major sources of uncertainty in emission inventories are:

- the accuracy of the underlying statistics (e.g., amount of cement production or battery consumption)
- the accuracy of emission factors (e.g., the mercury concentration in the coal that is burned in a specific location or country, or the quality of ore from a specific mine)
- assumptions about technology both for production means and for mercury pollution control (e.g., whether mercury is used in gold production or how much of it is recaptured after such use)
- assumptions about various practices (e.g., the prevalence of waste incineration)
- the degree to which national practices are similar in countries without national emissions data compared with those for which such data are available.

As discussed in the next section, changes in some of these parameters can greatly alter estimates of national emissions totals, without any

Uncertainty of Hg emission estimates by sector.

Industrial source	Uncertainty ( $\pm\%$ )
Stationary fossil fuel combustion	25
Non-ferrous metal production	30
Iron and steel production	30
Cement production	30
Waste disposal and incineration	As much as 5x
Mercury and gold production	?

Uncertainty of Hg emission estimates by continent.

Continent	Uncertainty ( $\pm\%$ )
Africa	50
Asia	40
Australia	30
Europe	30
North America	27
South America	50

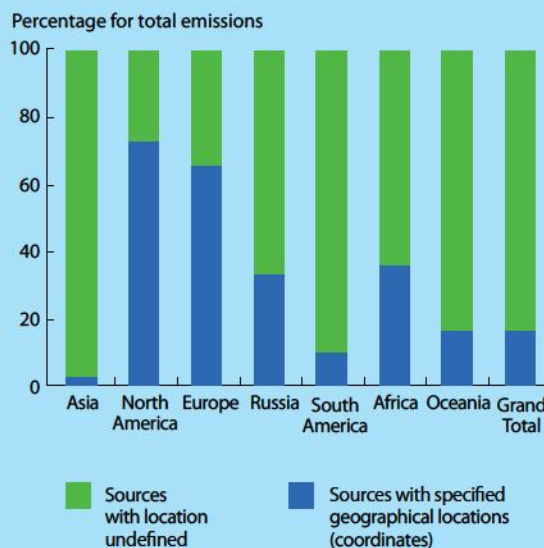
real change in the actual emissions themselves. Despite the uncertainties involved, at the global scale, emissions data still provide a picture of regional and national patterns and give insight into trends.

The quality of the information on emissions available in Europe and North America is generally of better quality than the corresponding information from other continents.

## Geospatial distribution of emissions

In order to model mercury concentrations and deposition it is not only necessary to know how much mercury is emitted but also where these emissions take place. Ideally, emissions data are reported together with information about the location of the emissions – as the graphic shows is the case for many point source emissions in Europe and North America. In most other parts of the world this information is lacking and so national emission totals have to be ‘geospatially distributed’ using some appropriate ‘surrogate parameter’ for which information is available. For example, population distribution is likely to provide a reasonable estimate of where mercury is consumed and thus where mercury emissions from waste disposal are concentrated. This process introduces further sources of uncertainty that can be reduced by improved data reporting. The global distribution of anthropogenic mercury emis-

sions in 2005 presented in the map on the previous page shows the results of ‘geospatial distribution’ of reported and estimated national emissions data to a 0.5 degree latitude/longitude grid.





# 4 Trends in mercury emissions estimates

Global emission inventories for anthropogenic mercury have been developed for various years in the past. These inventories utilized the best methods and data at the time when they were produced, based on the best available knowledge at that time concerning emission factors and the statistical data for production of industrial goods and the consumption of raw materials. The inventories were not produced, however, with the explicit goal of monitoring trends and thus should be used cautiously for that purpose. For 1990, 1995, and 2000, the methods were reasonably consistent, producing generally comparable data. In some cases, better data became available for some countries, typically as a result of a focused study examining mercury releases. The 2005 estimates, described in the previous section, used methods that have been revised along with new data. The result is that the 2005 estimates are not directly comparable to prior years, although when the revised methods and new data are taken into account, they offer some insight into recent trends. Regional differences in trends are also important to consider, particularly as emissions are increasing in some regions and decreasing in others.

## Trends until 2000

On a global scale, annual emissions in 1990 were estimated at 1881 tonnes. Estimated emissions rose to 2235 tonnes by 1995, but decreased slightly by 2000 to about 2190 tonnes. Europe had the greatest decrease, in part as a result of major changes in production and consumption in Central and Eastern Europe. North American emissions also declined significantly over the decade. Other regions increased, with Asia contributing the majority of the increase. From 1990 to 1995, Asian emissions rose by more than half, with half of that increase coming from China. Emissions from Africa also increased sharply from 1990 to 1995, but more modestly after that. South America and Australia, which had lower levels of mercury emissions to begin with, showed modest increases.

In Europe, the decreases were in part a result of far-reaching economic changes following the breakup of the Soviet Union and resulting political and economic changes there and in Eastern Europe. For a period, industrial production and consumption declined in Eastern Europe, and to some degree, improved control measures were implemented when production later increased. In Asia, the increase reflects a growing population and surging economic activity. In the first half of the 1990s, demand for electricity and heat rose sharply. In the second half of the decade, mercury emissions rose at a lower rate, perhaps as a consequence of a stabilizing demand for energy. New power plants were also being equipped with pollution control devices, including sulphur controls that also help remove mercury. Estimated emissions from China showed a slight decline from 1995 to 2000. At the same time, small-scale uses of coal for household cooking and heating increased resulting in greater emissions from that sub-sector.

## From 2000 to 2005

Comparing emissions estimates between 2000 and 2005 must be done with caution. Two major changes, along with many minor ones, have occurred in the methods and data used to calculate global anthropogenic emissions. First, the 2005 inventory of 1930 tonnes includes about 450 tonnes of emissions from sectors or activities that were not included in previous inventories. For example, artisanal/small-scale gold mining produces an estimated 350 tonnes of atmospheric emissions. While the source is not new, its inclusion in the global emission inventory makes the 2005 estimate appear higher than it otherwise would have in comparison with previous years.

Second, better information has improved estimates for some countries. For example, estimates of releases from South Africa in 2000 assumed that mercury was used in large-scale gold mining and processing. Recent, first-hand information



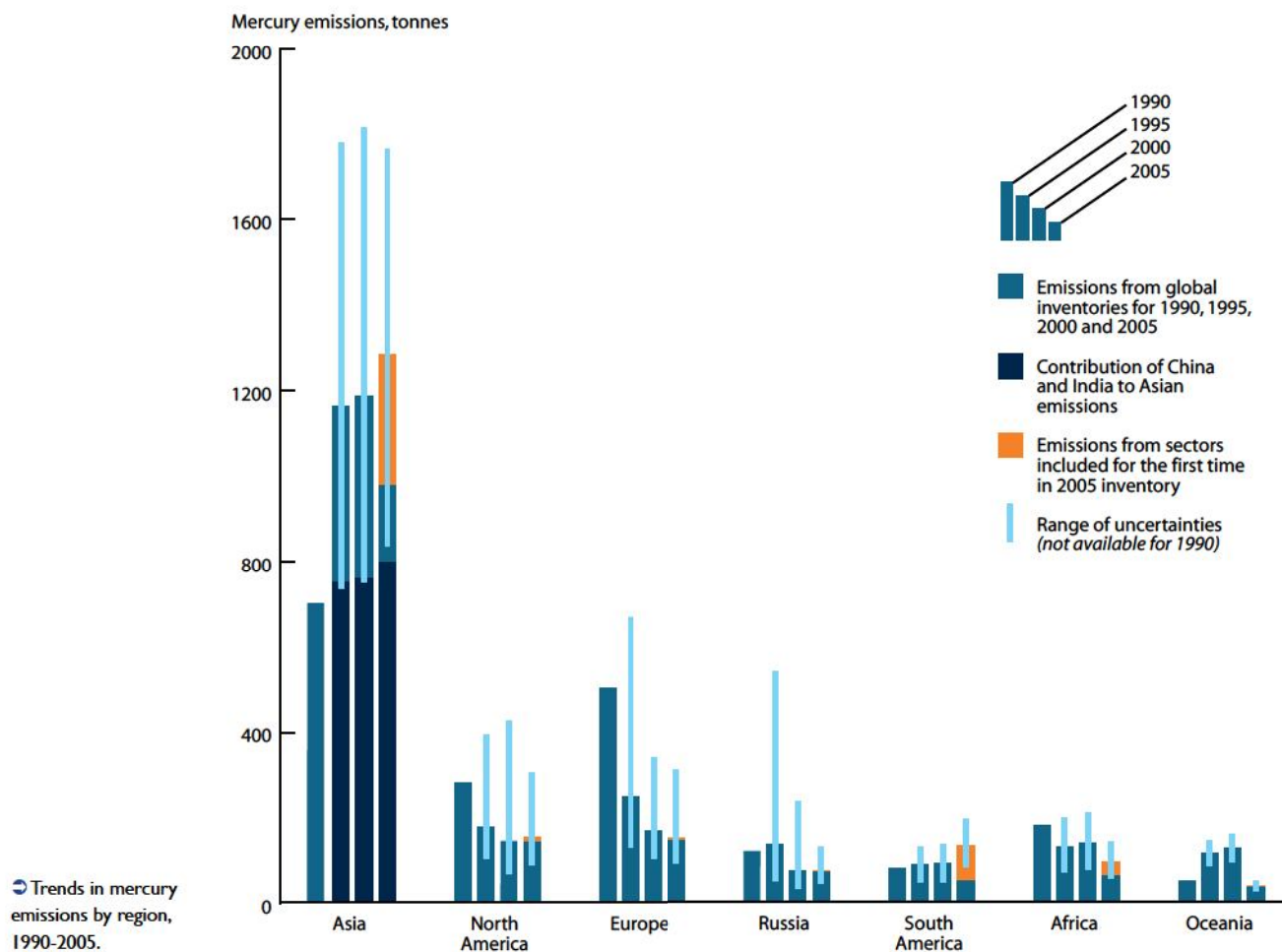
from South Africa, however, indicate that their gold mining processes do not involve mercury. As a result, mercury emissions from this important sector of the South African economy were about 100 times lower than had been estimated previously, reducing the national emission estimate by 150 tonnes. Similarly, data on the mercury content of Australian coal has cut emission estimates from that sector from 109 tonnes to 18 tonnes. These two changes alone produce an apparent (but not actual) emissions decline of 240 tonnes, or more than 10% of the global figure.

One big improvement has been the availability of mercury emission data from more countries, including some of those in the top ten list shown in the previous section. The UNEP focus on mercury is partly responsible for this step forward and data for two countries (Chile and Cambodia) reflected the first delivery of information utilizing the UNEP Chemicals Division 'Toolkit' for Identification and Quantification of Mercury Releases. The Philippines and Burkina Faso are in the process of developing mercury emissions data

using Toolkit. As was the case for South Africa and Australia, national data are more likely to reflect knowledge of specific local details that may be unavailable or unfamiliar to researchers working with global statistics.

For other countries, specific details of production methods and fuel use have also allowed for more accurate estimates of mercury emissions. This is especially important for the production of metals and for cataloging the amounts and types of fuel used in various economic sectors. These data were especially useful for updating emission estimates for countries in Africa and South America, continents for which few direct mercury emission data were previously available. The combination of these improvements is largely responsible for the apparent decline in emissions in Asia, Africa, Australia, and South America between 2000 and 2005.

In summary, however, global anthropogenic emissions of mercury to the atmosphere appear to have declined further by 2005 compared with 2000. The 2000 inventory can be revised to take







into account documented revisions to emissions estimated from some specific countries where new information has become available. With these revisions, equivalent sectors for which there is data in both years can then be totaled. This gives a figure for total global anthropogenic emissions in 2000 of around 1930 tonnes, compared with that in 2005 of around 1480 tonnes. The remaining emissions in 2005 of around 450 tonnes are associated with sectors that were not included in the 2000 inventory. Some of the decline in estimated emissions is indeed likely to reflect actual decreases in emissions, such as the result of emission control measures put into practice for some sources in some regions. Some of the apparent decline, however, is also likely to be the result of improved methods or better information for estimating emissions.

Coal burning power station.



In Europe, mercury emissions declined largely as a result of improved control measures. These improvements resulted from European Union directives and also implementation of the United Nations Economic Commission for Europe's Convention on Long-range Transboundary Air Pollution (UNECE LRTAP Convention) Protocol on Heavy Metals.

Electric filter, cement plant Leimen, Germany.



Estimated emissions for China, the United States, and Russia, did not change substantially from 2000 to 2005. In China, new data suggested that mercury emissions from coal combustion were lower than previously estimated, which in turn was offset by increases in industrial production activities in other sectors. Still, China's overall mercury emissions estimates increased during this period from around 605 to 635 tonnes for those sectors that were included in 2000. Emissions estimates for India similarly increased from around 150 to 160 tonnes from 2000 to 2005. Japan, on the other hand, exhibited substantial declines in estimated mercury emissions, with decreases in almost all sectors.

Although the changes in estimation methodology may obscure some of the actual emission changes from 2000 to 2005, they have nonetheless greatly improved understanding of mercury emissions worldwide, especially outside Europe and North America. The involvement of national emission experts from many countries has also helped provide important local details on specific industrial processes, quality of materials, and the spatial distribution of mercury-emitting activities, enhancing the accuracy of atmospheric models of mercury transport and deposition.

Rapid expansion of some economies has increased demand for cement, production of which is an important source of mercury emissions to air.



## Future scenarios

Future global mercury emissions are dependent upon a great many variables: the development of national and regional economies, development and implementation of technologies for reducing emissions, possible regulatory changes, and also factors connected to global climate change.

As a first attempt to investigate some of these aspects at a global scale through the year 2020, three general scenarios were used. The intent of these scenarios is not to present an accurate and detailed projection of the future, but simply to begin to explore the prospects for reducing mercury emissions. The estimates of future emissions are rough. For example, uniform rates of increase in production or consumption have been applied within a given region, despite the fact that substantial national differences may exist in mercury emission controls within the different countries in that region. Nonetheless, the general picture provides some insight into the degree to which national and international action can be effective.

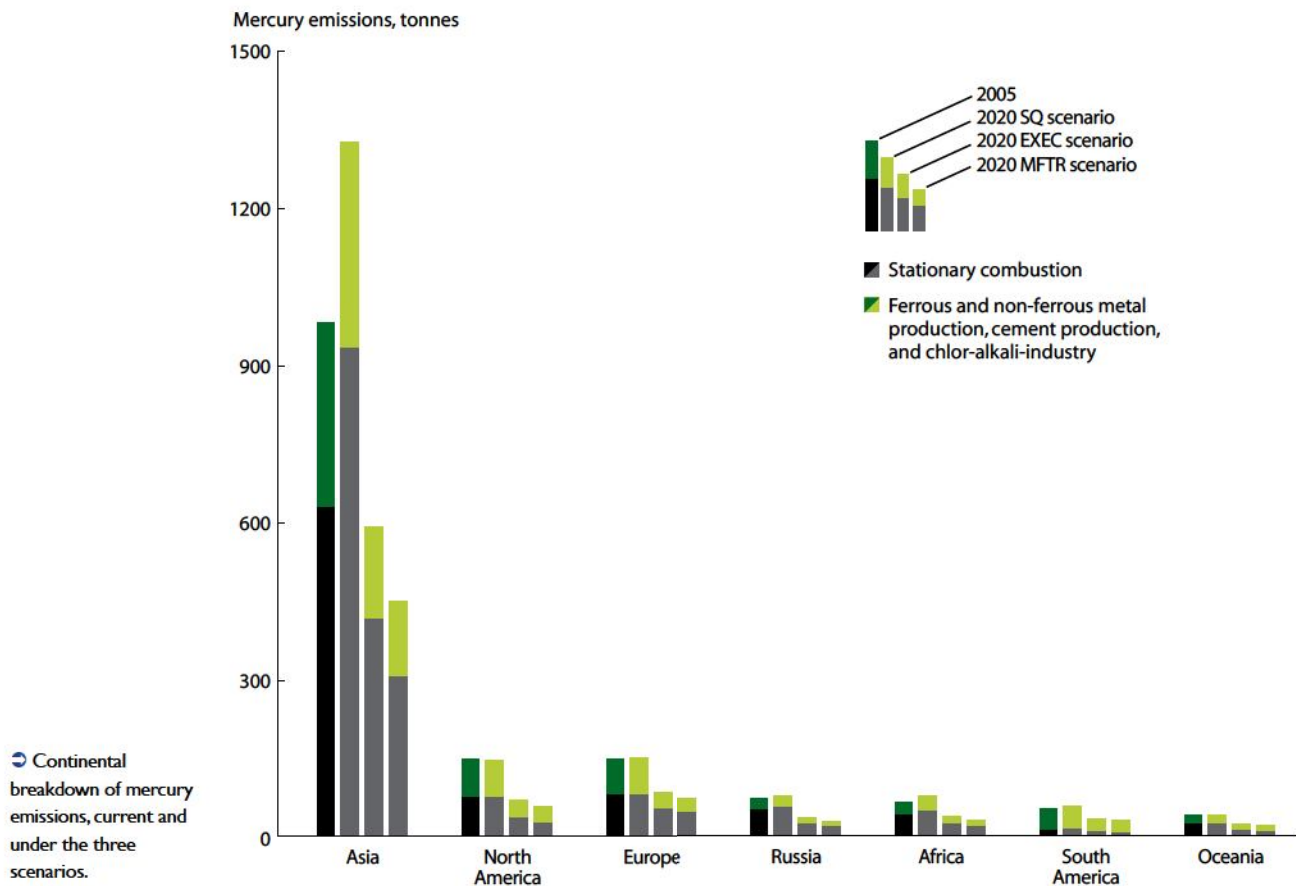
The first scenario assumes that current patterns and uses related to mercury emissions will continue, the “status quo” scenario. This scenario is based on an increase in economic activity, including in those sectors that produce mercury emis-

sions, but no change in emission control practices.

The second scenario assumes that mercury emissions control measures practiced or committed to in Europe are extended around the world, the “extended emissions control” scenario. This one incorporates trends in the use of mercury-reducing technology as well as the expectation that countries will meet current international agreements, including those requiring reductions in greenhouse gas emissions (and thus reductions in fossil fuel consumption, which also reduce mercury emissions).

The third scenario assumes that all available steps will be taken to reduce mercury emissions, the “maximum feasible technological reduction” scenario. Under this scenario, the cost of putting mercury control measures into practice is a secondary consideration, with the primary emphasis on technological feasibility.

For all three scenarios, a number of assumptions have been made about economic activity and other factors. Statistical data were only available for some countries and some sectors, in particular for Europe and North America as a result of recent research studies. Consequently, projections for other countries and for certain sectors have been extrapolated from the available data.





While these assumptions introduce additional uncertainties into the projections, the assumptions have been applied consistently across all data sets. In all three cases, too, the potential impacts of global climate change on mercury transformation, transport, and deposition have not been considered. Furthermore, these three scenarios consider only some of the sectors responsible for mercury emissions, totaling 1480 tonnes in 2005.

The results of the scenarios suggest that, under the “status quo” scenario, mercury emissions rise by the year 2020 to 1850 tonnes, an increase of about one quarter. Under the “extended emissions control” scenario, global mercury emissions in 2020 are projected to drop to 850 tonnes by 2020, or about half of “status quo” emissions. Under the “maximum feasible technological reduction” scenario, emissions are projected to drop to 670 tonnes by 2020, or two-fifths the “status quo.” The results should be treated with some caution. For example, a major contributor to the declines in the latter two scenarios is a reduction in emissions from coal burning, a result of both less coal being burned and better pollution control technology being applied to coal-burning facilities. Should these reductions not take place, mercury emissions are still projected to decrease in other major emission

sectors, but the overall reduction will be smaller. While there are other uncertainties for other emissions categories, the results nonetheless suggest that national and international action can yield substantial reductions in mercury emissions.

Geographically, both the “extended emissions control” and “maximum feasible technological reduction” scenarios predict marked declines in emissions on every continent (though possibly as a result of extrapolating results from one continent to another). Here, too, the results should be examined carefully. If, for example, expectations about the efficiency of pollution reduction measures in Chinese power plants are overstated by 50%, then mercury emissions from China may actually increase, in contrast to a 24% or 46% decline projected in the “extended emissions control” and “maximum feasible technological reduction” scenarios, respectively.

Realistic emission scenarios for the intentional use of mercury are difficult to prepare due to the lack of sufficient information on trends. Suitable substitutes are available for many products which makes the potential for emission reductions large. For artisanal gold mining, the potential for emission reduction is large but whether or not actual reductions are realistic is uncertain.

Main assumptions applied for some sectors under the three scenarios.

Sector	Status quo (SQ) 2020	Extended emissions control (EXEC) 2020	Maximum feasible technological reduction (MFTR) 2020
<b>Large combustion plants</b>	Increase in coal consumption in Africa (20%), South America (50%) and Asia (50%). Application of current technology	SQ 2020 assumptions plus: De-dusting: fabric filters and electrostatic precipitators operated in combination with FGD. Activated carbon filters. Sulphur-impregnated adsorbents. Selenium impregnated filters.	SQ 2020 assumptions plus: Integrated gasification combined cycle (IGCC). Supercritical polyvalent technologies. 50% participation in electricity generation by thermal method.
<b>Iron and steel production</b>	Application of current technology.	In sintering: fine wet scrubbing systems or fabric filters with addition of lignite coke powder. In blast furnaces: scrubbers or wet ESPs for BF gas treatment. In basic oxygen furnace: dry ESPs or scrubbing for primary de-dusting and fabric filters or ESPs for secondary de-dusting. In electric arc furnaces: fabric filters and catalytic oxidation.	EXEC 2020 techniques in existing installations plus: Sorting of scrap. New iron-making techniques. Direct reduction and smelting reduction.
<b>Cement industry</b>	Increase in global cement production (50%).  Application of current technology	SQ 2020 assumptions plus: De-dusting: fabric filters and electrostatic precipitators.	SQ 2020 and EXEC 2020 assumptions plus: All plants with techniques for heavy metals reduction.
<b>Chlor-alkali industry</b>	Phase-out of mercury cell plants by 2010		





# 5 Atmospheric transport and processes of mercury

The movement of mercury in air is determined by chemistry and by physics. The chemical properties of mercury, the specific form in which it is found, and the chemistry of the particular air mass all influence the length of time mercury remains in the atmosphere and the ways in which it is deposited. The physics of air circulation govern the pathways that mercury follows through the atmosphere. The basic principles of mercury chemistry and atmospheric physics are understood, but what takes place in the atmosphere is complex and further study is needed to understand in greater detail what actually occurs. Observational data of mercury are essential to test models of mercury transport and deposition. The precise chemistry of the mercury in the air is critical to understanding how it is deposited and how it is taken up by plants and animals.

## Mercury chemistry in the air

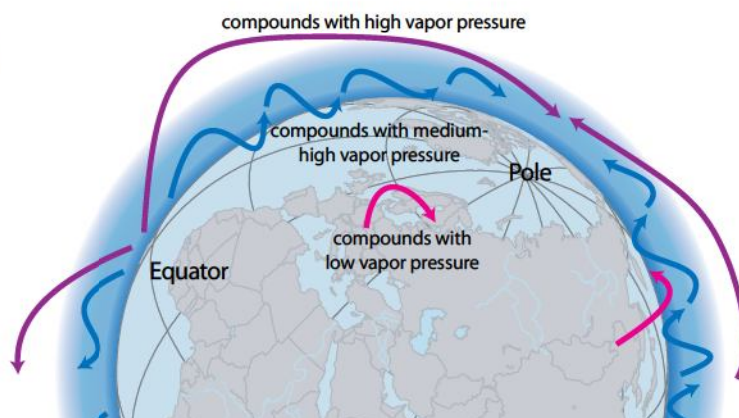
Most mercury in the air is in the form of gaseous elemental mercury. This form of mercury is estimated to stay in the atmosphere from six to 18 months. This 'atmospheric lifetime' allows for it to be transported over long distances and it is thus found throughout the troposphere (lower atmosphere) in relatively consistent 'background' concentrations. Mercury is also emitted in oxidized forms. Some of this is in gaseous form, referred to as reactive gaseous mercury. Some of it is bound to particles and thus termed total particulate mercury. Both forms of oxidized mercury are deposited relatively quickly from air, typically within hours or days of release or formation, though the mercury may be re-emitted in elemental form. The reactive forms of mercury are less likely to travel far, making their primary effects regional rather than global. However, under favourable atmospheric conditions, even particle-associated mercury can be transported large distances (i.e., between continents). The transformation of gaseous elemental mercury into forms that are more readily deposited is poorly understood. There are several candidates,

such as bromine, ozone, and the hydroxyl radical, that may be involved in the oxidation of elemental mercury to form reactive gaseous mercury or total particulate mercury in the atmosphere.

Once reactive gaseous mercury or total particulate mercury has been deposited, the mercury is likely to undergo additional reactions. Mercury can also be transformed by bacteria into methyl mercury, which is more toxic. Various chemical reactions can return mercury to the elemental form which can be readily re-emitted. By this process, mercury that has been deposited can be re-emitted and continue travelling through the atmosphere from source regions to receptor regions in a series of 'hops'. This process is known as the grasshopper effect, allowing pollutants to travel farther than might be expected from their usual residence times in the air. One result of this transport is that mercury (like many other air pollutants) may be accumulated in the polar regions, where conditions may be less favourable for re-emission. Furthermore, special conditions that occur in polar regions in springtime (after polar sunrise) have been shown to enhance deposition, depleting the mercury in the lower atmosphere.

Measurements of air concentrations are important indicators of underlying chemical and

Even after it has been deposited, mercury can be re-emitted, allowing it to be transported over long distances in a series of 'hops'.





physical processes. Levels of gaseous elemental mercury are typically between 1.1 and 1.7 nanograms per cubic meter in areas remote from large sources in the southern and northern hemisphere, respectively. In East Asia, the regional atmospheric level is as high as 4 nanograms per cubic meter. Locations close to sources, such as near an old silver mine at Almaden, Spain, have reported peak atmospheric levels as high as 5 micrograms per cubic meter, or over a thousand times higher than the relatively high background levels in East Asia. High levels of reactive gaseous mercury highlight the polar effect, where concentrations in the Arctic can on occasion be five to fifty times higher than levels measured in Europe and North America.

Among the important questions to be answered about mercury chemistry in the air is the nature of reactive gaseous mercury. The exact composition of reactive gaseous mercury is also important for estimating deposition rates and also for assessing its fate in the food web.

## Regional patterns

As noted above, special conditions in the polar regions lead to rapid deposition of mercury in spring. The depletion of mercury from Arctic air was first observed in the 1990s. Considerable field and laboratory research since then has established that bromine and sunlight are essential to this process. Bromine enters the air when open leads freeze, and the ice formation pushes bromine ions out. The necessary conditions occur during spring, when temperatures are below  $-4^{\circ}\text{C}$  and the sun is above the horizon. Furthermore, the chain of reactions involving bromine and gaseous elemental mercury are temperature dependent. Compounds at intermediate stages in the chain are stabilized at colder temperatures and thus more readily allow the reactions to take place in the cold.

Arctic mercury depletion events have been estimated to increase the deposition of mercury north of the Arctic Circle from an expected 80 tonnes per year to around 200 tonnes per year. The significance of these events, however, is still in question. High levels of mercury have been measured in snow in Arctic areas near the ocean, but the level in snow decreases rapidly after the deposition events and gaseous elemental mercury increases, indicating that much of the mercury may be re-emitted rapidly. Recently, patterns of atmospheric mercury depletion resembling Arctic mercury depletion events have been observed at

sites on the Norwegian mainland, on the Greenland ice sheet (at high elevation and remote from the sea), and on Mount Bachelor in western USA, opening new aspects of the chemical processes responsible for these events.

In temperate and tropical latitudes, bromine may still be the key to oxidation of gaseous elemental mercury on a large scale. Here, though, the reactions are slower due to higher temperatures, but the process is more continuous than episodic as is the case in the Arctic. Relatively small variations in background gaseous elemental mercury concentrations are seen outside the polar regions. High-altitude reactions may also be important, but are less well understood. Over the continents, bromine is also present from sources such as coal burning and forest fires. Less is known, however, about the reactivity of this bromine.

There is greater uncertainty about the reactions involving total particulate mercury, in part because, like reactive gaseous mercury, it is not clear what compounds comprise total particulate mercury and also because of the number of processes by which mercury may be transformed to total particulate mercury. Although there is evidence to support a major role for bromine in atmospheric mercury chemistry, a substantial role for ozone in transforming gaseous elemental mercury cannot be ruled out.

## Deposition and re-emission

Levels of mercury in air are, except for locations close to major sources, too low to be of direct concern to people or animals. The problem comes when mercury is deposited and enters the food web. Because mercury is transported throughout the world, even remote, pristine areas can be at risk from mercury pollution. The re-emission of mercury is an additional complication, because any given location can be simultaneously a receptor of and a source of mercury.

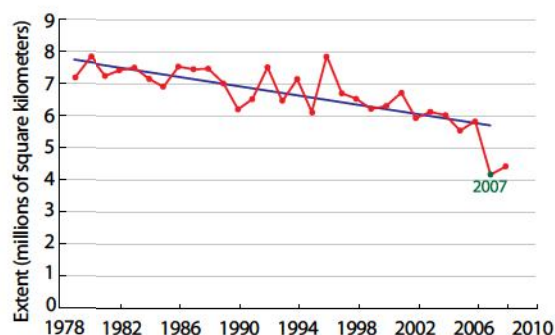
The reactive gaseous mercury and total particulate mercury that are emitted directly from anthropogenic sources may be made up of different compounds than the reactive gaseous mercury and total particulate mercury that are formed from gaseous elemental mercury. Consequently, reactions and deposition close to sources may be different from those farther away. Such differences are important factors in determining rates of deposition, which can involve chemical reactions with the surfaces or waters, and what happens to



the mercury once deposited. Despite the significance of reactive gaseous mercury chemistry, only one study has examined reactive gaseous mercury deposition. Similarly, only a few studies have addressed the fate of mercury after deposition. These studies suggest that oxidized mercury is in part reduced to the elemental form, allowing for re-emission. Furthermore, they suggest that surface chemistry is a key factor in determining global circulation and budgets of mercury. Thus, more research is needed to understand what happens between deposition and re-emission.

## Impacts of climate change

Global climate change is expected to alter the conditions under which many reactions involving mercury occur. Higher ocean temperatures and reduction of sea-ice cover in polar areas may result in greater emissions and re-emissions from the seas, altering the balance between marine and atmospheric mercury levels that currently exists. Climate change and economics are also likely to alter human consumption patterns. Rising oil prices may lead to greater use of coal for generating electricity, resulting in greater mercury emissions. If other means of energy production are used, such as nuclear energy or wind power, then mercury emissions could decline. Predicting the net impacts from climate change and changes in energy consumption and fuel use is thus very difficult, but nonetheless important to keep track of in order to better understand and control emission levels.



A decrease in Arctic sea-ice extent is just one of the results of climate change that could affect mercury cycling in the atmosphere.



Changes to clean energy production could reduce mercury emissions, however if future energy demand is met by increased coal burning, mercury emissions are likely to increase.





# Measured mercury concentrations and deposition

Since the start of the industrial age, mercury levels in the environment have risen. Some of these changes may be the result of ecosystem changes. Higher biological productivity in Arctic lakes, for example, has led to greater retention of mercury over time as the mercury is captured in biota rather than re-emitted. Nonetheless, anthropogenic emissions are responsible for much of the observed increase worldwide. Mercury monitoring is expanding around the world, providing more information and allowing scientists to assess atmospheric trends over the past two or more decades.

## Methods for monitoring mercury trends

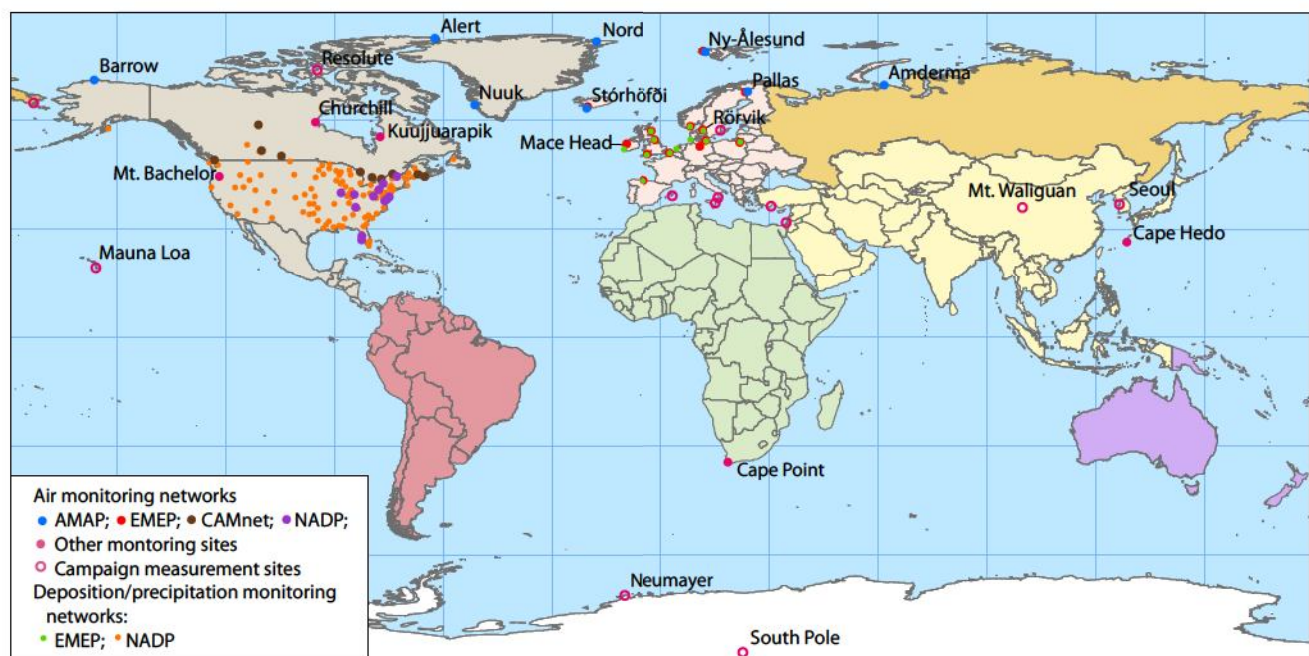
To help monitor mercury trends, there are several regional and national atmospheric mercury monitoring networks around the world. These include the Arctic Monitoring and Assessment Programme (AMAP), the LRTAP Convention's European Monitoring and Evaluation Programme

(EMEP), and the Canadian Atmospheric Mercury Measurement Network (CAMNet). The most extensive monitoring to date has been in Europe and North America. More recently, stations have been set up in China, Japan, and South Korea. The southern hemisphere, by contrast, has only one station, where atmospheric mercury is continuously monitored, at Cape Town, South Africa.

## Map of the stations in monitoring networks

Initially, mercury monitoring focused on wet deposition. Later, direct measurements of gaseous elemental mercury have been added, initially using manual systems, but more recently using automated systems capable of monitoring gaseous elemental mercury with higher time resolution. Monitoring of reactive gaseous mercury and total particulate mercury has been carried out in a few short campaigns in recent years, but ongoing monitoring of these fractions of mercury is just started recently at a few places.

Background air monitoring networks and stations around the world that monitor mercury.





## Archives

Even the longest-running mercury monitoring programmes can only provide data on air concentrations and deposition of mercury for the last 15 to 20 years. Other techniques are required for evaluating longer-term trends in environmental mercury. Natural environmental archives such as lake sediments, peat, and ice cores are the only link between current and past deposition to and accumulation in terrestrial and aquatic environments. These archives provide a useful means of reconstructing the atmospheric load on a local, regional, and global scale.

The differences between archive samples from pre-industrial times and those from the present are of particular interest as they reflect the influence of anthropogenic sources on pre-existing natural circulation of mercury. In both peat cores and lake sediment cores, a clear increase in mercury concentrations is observed today compared with the pre-industrial period, though the magnitude of this increase differs between these two media.

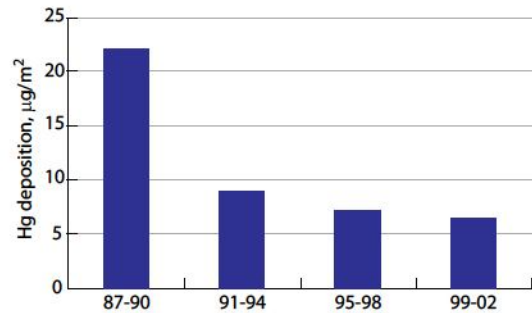
From pre-industrial times to today, mercury levels in sediments have generally increased by a factor of about three. In general, levels in sediments peaked between the 1970s and 1990s, which is consistent with global emissions data and with the results from box models (see Section 7). Mercury levels in peat were highest 10 to 20 years earlier.

## Wet deposition

The longest time series of measurements are available from Rörvik, Sweden which show a sharp

decline in wet deposition from the period 1987-90 to the period 1991-94, after which a smaller but steady decrease has continued. Today the level is two to three times lower than it was before 1990, corresponding to a decrease in regional emissions.

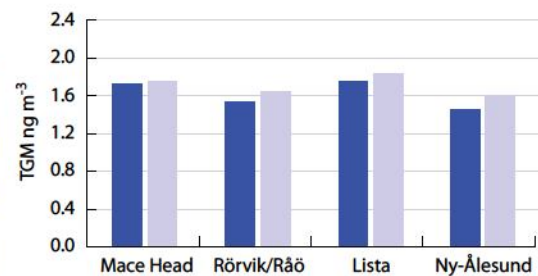
In Europe, the wet deposition of mercury has declined since the mid 90th and until today between 9 and 46 %. In North America a decrease of about 10% is observed in the concentration in precipitation. The decrease in both North America and in Europe is attributed to the decrease in local and regional emissions.



## Mercury concentration

Atmospheric mercury concentrations in North America have decreased during the last decade downwind of urban areas. For example, concentrations decreased by 17% close to Toronto and by 13% close to Montreal. In remote areas the decrease has been much smaller. At Alert in Arctic Canada, no trend has been observed. Most of the air masses at Alert come from Eurasia and though European emissions have decreased, they may have been offset by an increase in Asian emissions.

In Europe there has been a slight increase from the period 1995-98 to the period 1999-2002. Trends in remote locations in North America and Europe are explained by low local and regional emissions that make global emissions more important. These measurements are thus dominated by global background concentrations and not affected by changes in local and regional emissions.



Mercury wet deposition measured at Rörvik, Sweden.

Changes in Total Gaseous Mercury (TGM) at four sites in Europe from the period 1995-98 to the period 1999-2002.

Wet deposition sampler at Sequoia National Park Mercury Deposition Network station.





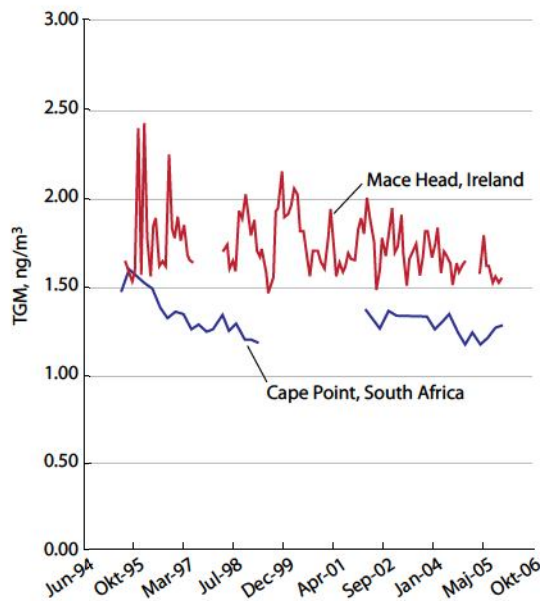
## Geographical variations

In China, which has become the largest source of anthropogenic mercury, most data are only available from short monitoring campaigns. The few long-term records indicate deposition increases in areas downwind from major source areas.

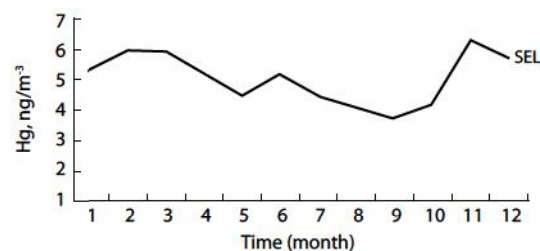
Data from ship cruises in the Atlantic show that marine air masses are typically low in mercury concentration. The highest levels recorded were when the ship was close to European sources in the North Atlantic. In the Northern Hemisphere the background atmospheric concentration of mercury is 1.5-1.7 nanograms per cubic meter and in the Southern Hemisphere the concentration is 1.1-1.3 nanograms per cubic meter.

Other studies have examined the profile of mercury concentrations as altitude increases through the troposphere. At high altitudes, levels were consistent across large areas, in keeping with the expectation that gaseous elemental mercury stays in the atmosphere for a long time. Close to the stratosphere (upper atmosphere), gaseous elemental mercury levels were lower, probably from the influence of bromine compounds produced at high altitudes. In the Arctic, gaseous elemental mercury levels were much lower close to the surface during spring depletion events. Higher up, the levels were similar to global background levels, as expected from understanding of the fast reactions involving bromine taking place close to the snow surface rather than throughout the air column.

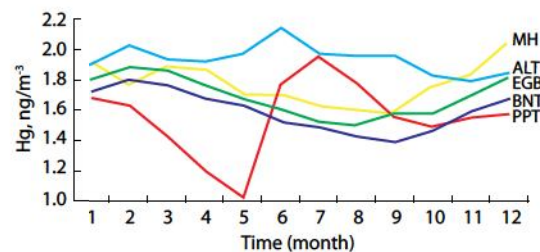
Looking to the future, the likely impacts of climate change on mercury transport and deposition are unclear. So far, changes in emissions have had a far greater impact than changes to temperature and other environmental parameters.



● Total gaseous mercury (TGM) at two stations, Mace Head (Northern hemisphere) and Cape Point (Southern hemisphere).



● Seasonal variation in Gaseous Elemental Mercury (GEM) measured at the Point Petre (PPT), Egbert (EGB) and Burnt Island (BNT) stations in Canada, Alert (ALT) in Arctic Canada, Mace Head (MH) in Ireland, and Seoul (SEL) in Korea. Note the change in scale on the SEL plot.







# Modelling of mercury transport and deposition

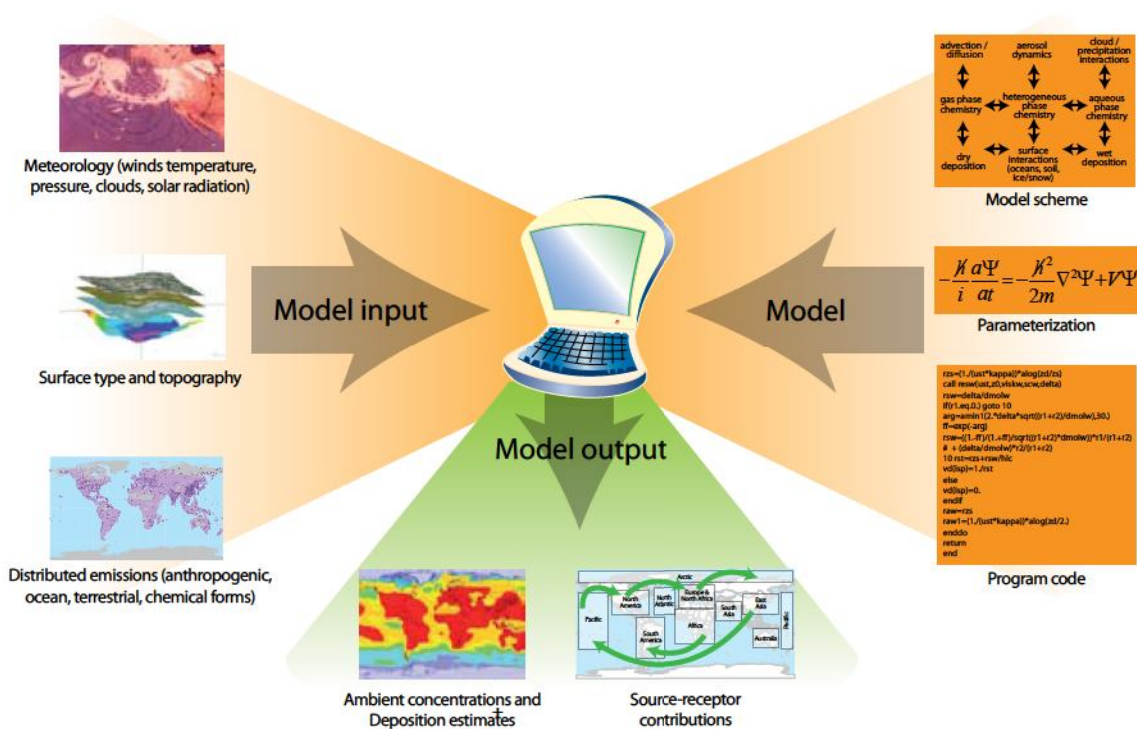
Measurements of mercury levels, whether at emission sources or in various locations and environmental compartments, are important in establishing the nature of mercury pollution. By themselves, however, such measurements offer only limited insight into large-scale transport patterns. Transport patterns are important for many reasons, not least of which are assessing which sources and source regions are responsible for observed pollution in specific areas, and evaluating scenarios for future changes in mercury pollution. For these and other reasons, various numerical models of mercury dispersion and cycling in the environment have been developed. All models have limitations, and mercury models must contend with uncertainties on many fronts, some of which were described in the previous sections. Nonetheless, modelling can provide useful information for both further research and to inform policy decisions.

## Model types and methods

Mercury models fall into two main categories: geographical transport models at various scales to examine transport and dispersion, and multimedia box models that describe cycling of mercury among environmental compartments. Each model type has its particular use, and some are run together to help capture different variables to improve accuracy.

Geographical transport models range in scale from local models for short-range dispersal from individual sources, through regional and continental models, to hemispheric and global models. With each increase in scale, the resolution of the model decreases in order to keep the calculations manageable. Several regional models have been developed for Europe and North America, with one additional model for East Asia. Not surprisingly, these models focus on regions with significant mercury sources. Hemispheric and global

Components of an atmospheric mercury transport model.





models are used to examine intercontinental dispersion and also for long-term simulations.

Box models apply a mass balance technique to examine, in simplified form, the exchange of mercury between air, soil, water, vegetation, and other compartments. These models use exchange rates determined by observations and experiments to simulate the flow of mercury from one compartment to the others. One advantage of these less computationally demanding models is that they are easier to run and thus can be run for time scales of several centuries, useful in evaluating long-term flows of mercury through the environment.

Most of the geographical transport models focus primarily on the atmosphere, because it is the most dynamic vehicle for mercury transport and because atmospheric deposition results in much of the mercury exposure for plants and animals. Some models also include interactions between the atmosphere and the surface of the sea and land. The box models typically include all components.

The models also incorporate chemistry to simulate the reactions that mercury is likely to undergo in the atmosphere. Some models are more explicit than others in their treatment of reactions in air and with surfaces. Similarly some models ignore re-emission whereas others attempt either to account for it indirectly or to model re-emission processes along with atmospheric ones. The models address deposition in various ways, including both wet deposition (mercury carried to the surface via precipitation) and dry deposition (direct deposit of airborne mercury onto surfaces). There are a variety of techniques used for each step in the modelling process, but all the models are constrained by the need to ensure that their results are at least generally consistent with observational data.

## Model applications

One of the main purposes of mercury models is to simulate the distribution of mercury through air transport and to use that information to simulate deposition patterns. Together, these results can illuminate source-receptor relationships. If deposition occurred close to sources, mercury pollution would be a local or regional issue. The global distribution of mercury, however, underscores that it is a global issue. Understanding the relative contribution from different sources is important to establishing where action is needed to control emissions and to reduce deposition. For example, if a region receives most of its deposited mercury from another region, action within the region will have only a modest impact

on mercury levels. Instead, action will be required in the source region.

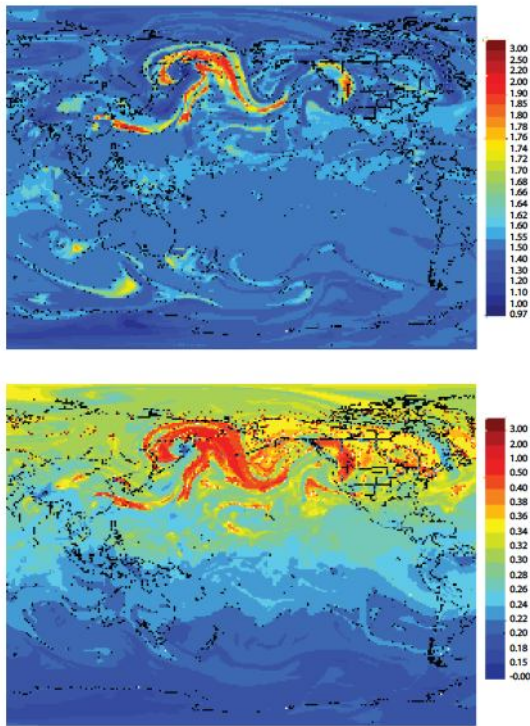
Global mercury chemistry can be examined through models to determine if various processes are compatible with existing observational data. By incorporating specific chemical reactions or pathways, the models can produce results that can be compared with empirical data. If the results are consistent with the observational data, then the reactions in question are a plausible description of the actual chemistry involved. If the results are inconsistent, then the reactions may not be playing a major role in atmospheric chemistry. This approach does not produce conclusive answers, but it is a cost-effective way to test new ideas prior to extensive fieldwork. A number of studies of this kind have helped improve understanding of mercury chemistry in the atmosphere, allowing models to better replicate observed data, thus increasing confidence in the modelling results.

Models can be used to provide a regional picture on the basis of a few observation sites. The Arctic mercury depletion events described earlier offer another important challenge for mercury models. First, the models must successfully capture the reactions between mercury and bromine, combined with the environmental conditions that stimulate the reactions. Second, the models must account for re-emission following deposition to snow. Third, the models must replicate the latitudinal pattern of deposition. One model can now reproduce the depletion events when they use bromine concentrations observed from satellites as one of the model inputs. Since Arctic observational data are limited to a few monitoring sites, the models provide a regional picture that would otherwise be missing.

Modelling can also demonstrate the importance of episodic phenomena, such as the long-range episodic transport that is a major contributor to trans-Pacific transport from East Asia to North America. Cyclonic activity, most active in spring, can lift mercury into the upper troposphere, where it can traverse the Pacific in only five to ten days. Such transport is significant because East Asia releases about half of global anthropogenic mercury. Observational data from the western United States and Japan suggested a strong and rapid flow of mercury eastwards from Asia. Modelling efforts were able to simulate the observed data. Using only Asian emission data, the models still reproduced the spikes in mercury levels in the U.S., demonstrating the contribution from Asian sources.

Model intercomparison offers a way to estimate the uncertainty in modelling and to highlight



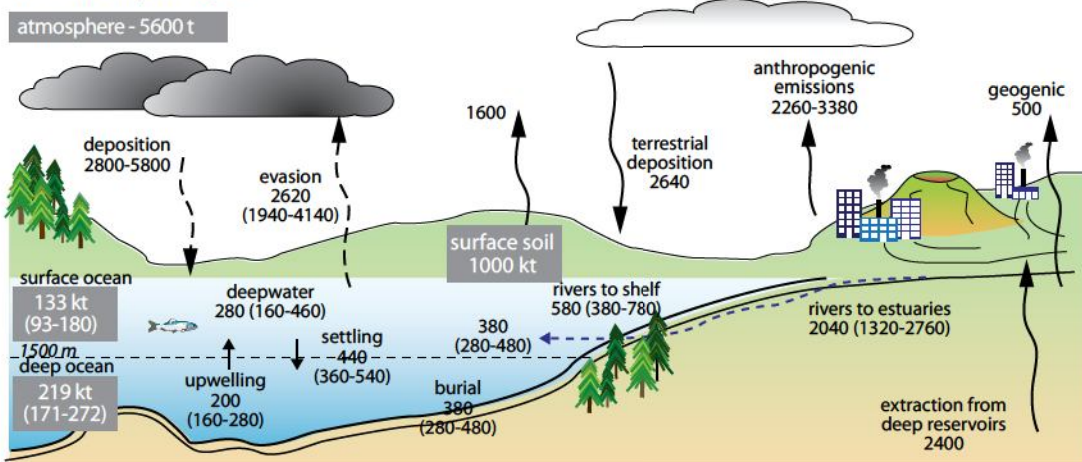


the significance of differences in the ways different models account for various processes. While observational data are important for constraining models, there are too few monitoring stations and too few data to evaluate model performance adequately. Intercomparisons allow the strengths and weaknesses of various models to be identified, leading to improvements in both understanding and modelling. Two major intercomparison studies have been conducted for global-scale models. Both have helped assess the sensitivity of the models to the input data and also the range of uncertainty associated with the results of the model runs.

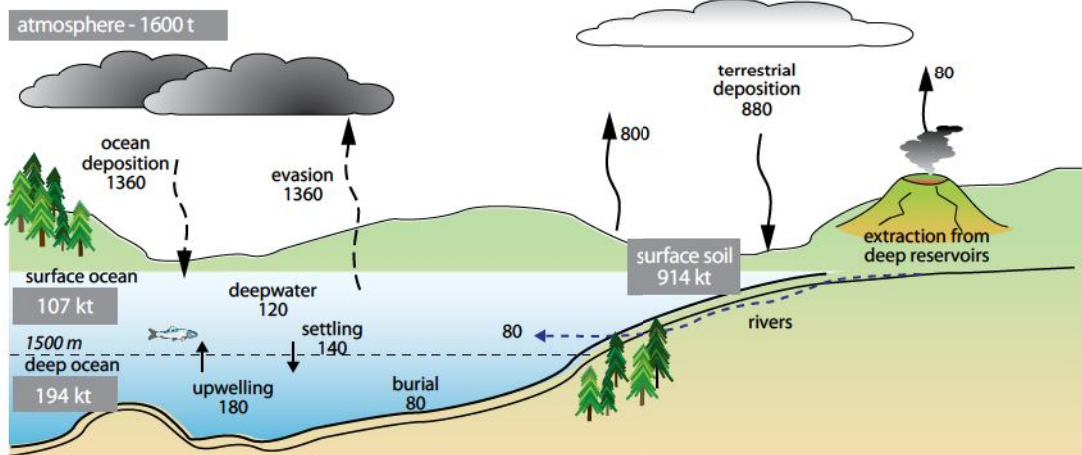
Mercury trends on various time scales can be analyzed through models. Geographical models use emissions data from various years to complement observational data, providing insights into trends on a decadal scale. On longer time scales, mass balance studies have used multi-media box models to compare mercury deposition in pre-industrial times with deposition today.

Model results showing episodic transport of mercury from East Asia to western North America. The upper panel shows the simulation for all emissions and the bottom panel the simulation for anthropogenic emissions from East Asia.

### Present-day budget



### Pre-industrial budget



Results of box models showing changes in mercury cycling from pre-industrial times to the present (all fluxes in t/yr).



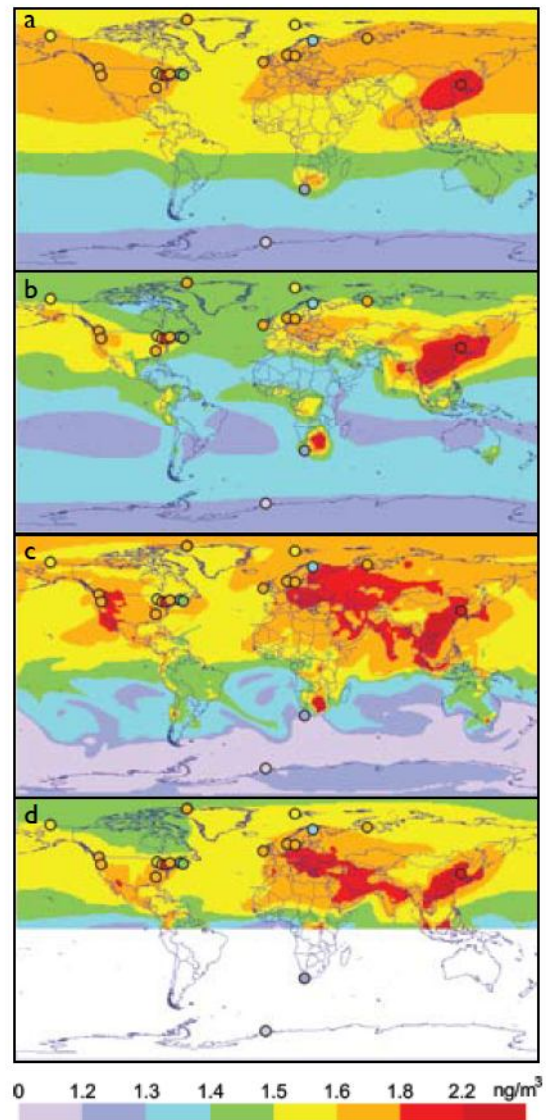
## Modelling results

Three global models and one hemispheric model (for the northern hemisphere) have been used in a modelling study to compare results for air concentrations and deposition patterns. The four models each used anthropogenic emissions data for the year 2000, combined with natural emissions estimates. Because some of the models adjusted the 2000 data for various reasons, the emissions estimates that were used in the models varied by more than a factor of two, from 4000 tonnes to 9230 tonnes per year. The relative contribution of anthropogenic sources ranged from 34–55%. Furthermore, each model used its own parameters for mercury chemistry, re-emissions, and interactions with other environmental compartments such as the ocean. Despite these differences, the results of the four models were within 15% of each other on a continental scale for the concentration of gaseous mercury in the environment. East Asia had the highest concentrations, whereas Australia had the lowest.

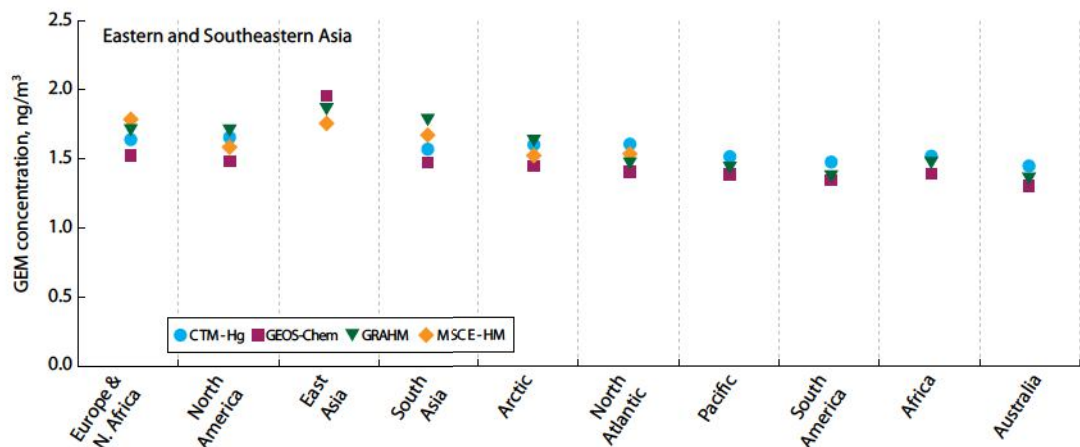
The models diverge to a greater extent when it comes to deposition. Both the spatial patterns and the amount of mercury deposited vary between models. In all models, East Asia had the highest deposition rates, whereas the lowest rates were over the oceans. The variation between models was on the order of a factor of two.

To better understand the discrepancies, the study separated wet and dry deposition. Wet deposition was simulated with reasonable consistency by all models, with the exception of deposition in the Arctic related to mercury depletion events. Estimates for deposition in temperate latitudes were fairly consistent. The agreement was greatest for regions where regular monitoring is most common, which is not surprising since those observational data are used to constrain the models. Dry deposition, by contrast, showed considerable variation between models. There are no systematic observations of dry deposition with which to constrain the models. Model results for dry deposition varied by the emissions estimates and other parameters

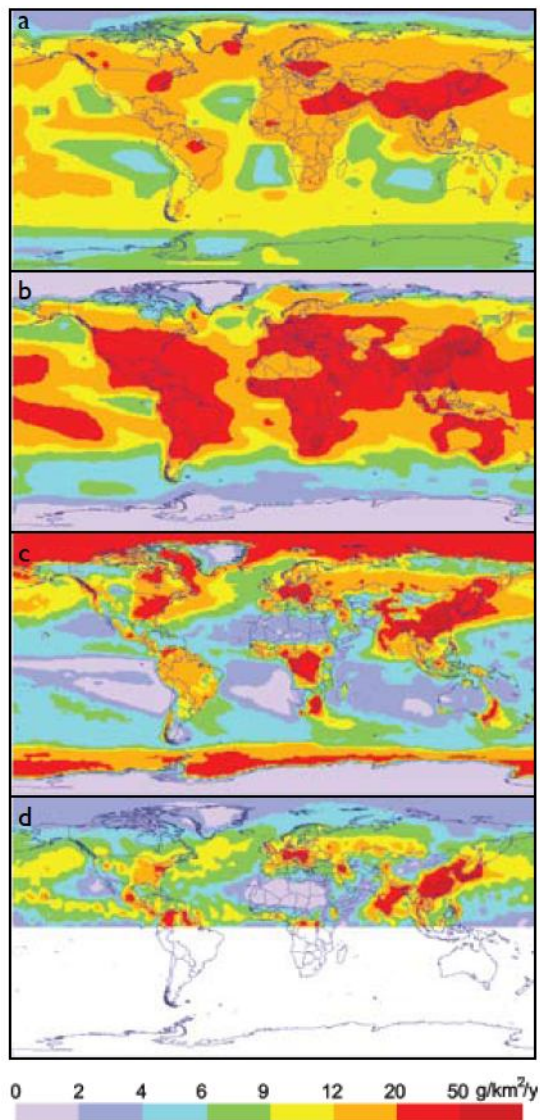
➡ Annual mean concentration of Gaseous Elemental Mercury (GEM) in ambient air in 2001 simulated by the (a) CTM-Hg, (b) GEOS-Chem, (c) GRAHM, and (d) MSCE-HM models, compared with long-term observations (circles). Despite the differences in spatial distributions, the absolute values of GEM concentrations predicted by the different models are not significantly different.



➡ Comparison of four different model simulations of average concentration of gaseous elemental mercury in different regions of the globe in 2001.







used by a particular model. More work is needed to improve understanding of dry deposition and the precise reactions by which elemental mercury is oxidized to compounds that deposit rapidly. Observational data are also essential, particularly

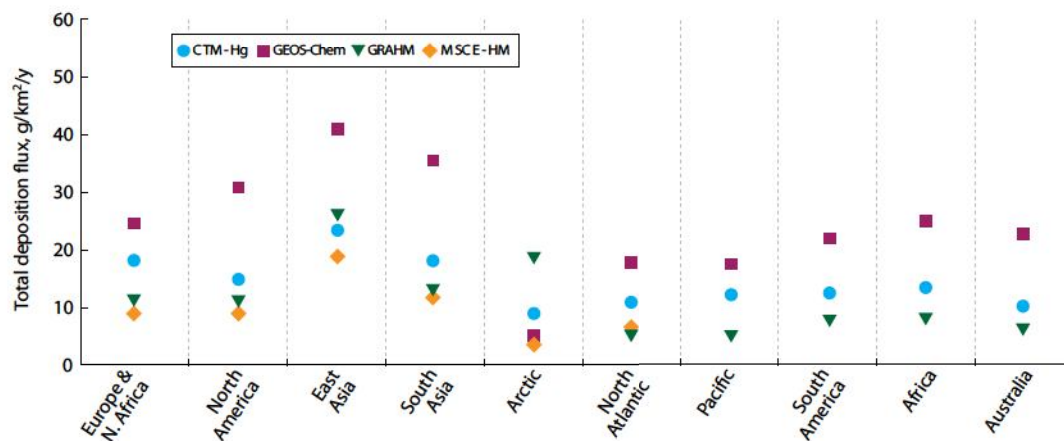
on concentrations of oxidized mercury compounds and on rates of wet and especially dry deposition.

The results of modelling source-receptor relationships show considerable variability among regions. One study found that North America received two-thirds of its mercury from natural sources or other regions (a quarter from Asia and about 14% from Europe) and about one third from anthropogenic sources within North America. Europe receives 40% of its mercury from outside the region, whereas Asia is responsible for two-thirds of its own mercury deposition. Another study had similar results, with North America responsible for a third of its own mercury deposition, with another third from natural sources and the remainder from other regions. By one model, episodic transport from East Asia was found to be responsible for about one-fifth of deposition in the western U.S.

An important use of models in this regard is the evaluation of the impacts of changes in emission rates. A sensitivity study involving four models examined the impacts of a 20% reduction in emissions in four major source regions: North America, Europe and North Africa, South Asia, and East Asia. (Note that a sensitivity study is designed to examine effects of various changes, but is not based on the likelihood of those changes occurring.) The available results show that a 20% emissions reduction in any of the source areas would typically have the greatest effect on deposition within that region. An exception may be North America. In the results from two of the four models, deposition in North America declined more from reductions in East Asia than from reductions in North America itself.

In addition to reduced deposition within the region, reductions in emissions from the source areas would produce lesser deposition reduc-

Mercury deposition in 2001 simulated by the (a) CTM-Hg, (b) GEOS-Chem, (c) GRAHM, and (d) MSCE-HM models.

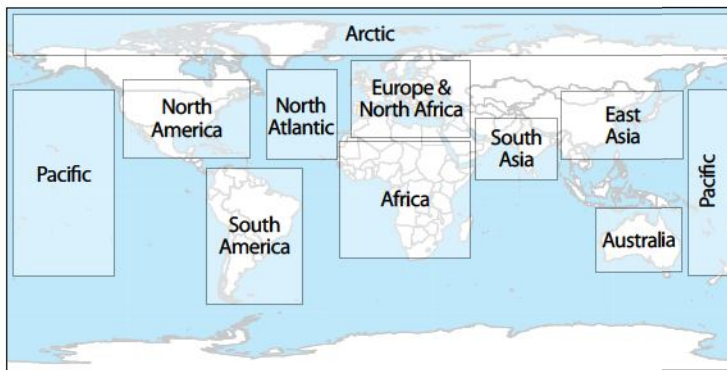


Comparison of four different model simulations of total deposition of mercury in different regions of the globe in 2001.

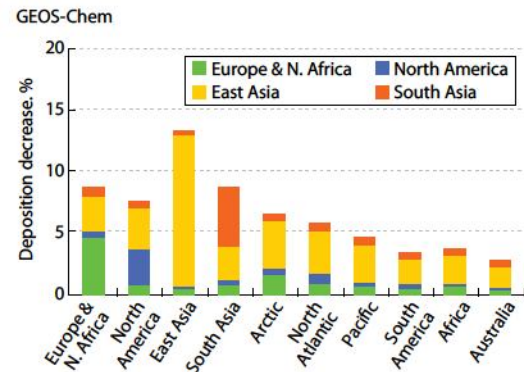
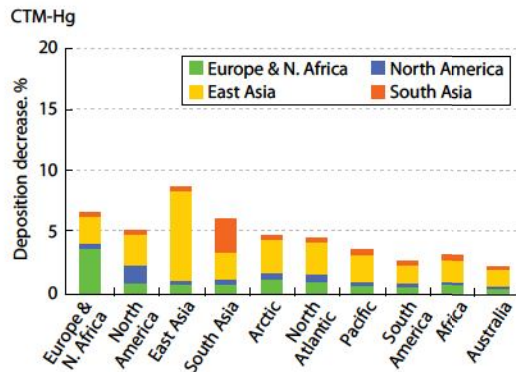


tions in other areas, including areas distant from the source regions such as Australia and South America. Reductions of 20% in East Asian emissions were found to have a much greater effect than reductions of the same percentage in the other three source areas. The areas outside East Asia that would experience the largest deposition reductions were the Arctic, the North Pacific, and northwestern North America, with lesser reductions spread farther away. Emissions reductions in the other three source areas had some effect on adjacent areas, but the deposition reductions were not nearly as substantial globally as those from reductions in East Asia.

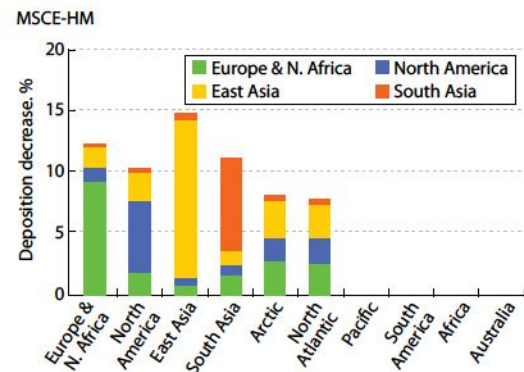
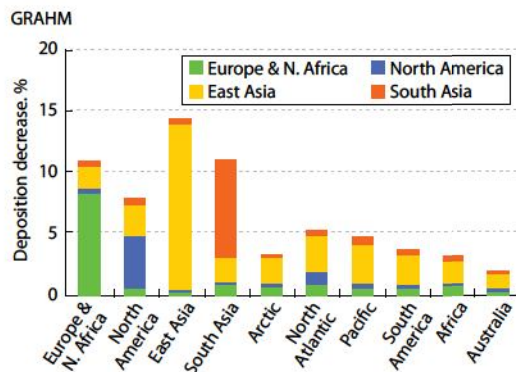
Location of receptor regions considered in the model analysis of transport between source and receptor regions.



A modelling study of decadal trends in mercury deposition in the northern hemisphere, using emissions data from 1990, 1995, and 2000, found that deposition in Europe declined by nearly half, due to emissions controls and the change in Eastern European countries from centrally planned to market-oriented economies. North America had smaller changes due to lower emissions and also a greater contribution from trans-Pacific transport. East and Southeast Asia, by contrast, increased slightly and became the highest deposition regions in the hemisphere, largely because of the sharp European decline. An analysis of the Bay of Fundy region in eastern Canada showed declining deposition, largely due to decreased emissions from incineration. Emissions from the U.S. and Canada contributed up to 50% of the deposited mercury in the early 1990s, but only about 30% by the late 1990s. Natural sources were responsible for some 14-32%, with the remainder coming from long-range transport. It is important that such studies take account of the changes over time in the way in which global inventories are compiled, which, as discussed previously, can significantly affect the inventory estimates.



Relative decrease in mercury deposition due to a 20% emission reduction in the four source regions simulated by four different models (CTM-Hg, GEOS-Chem, GRAHM, and MSCE-HM). Colouring on bars shows how much of the decrease is associated with the emission reduction in a given source region.





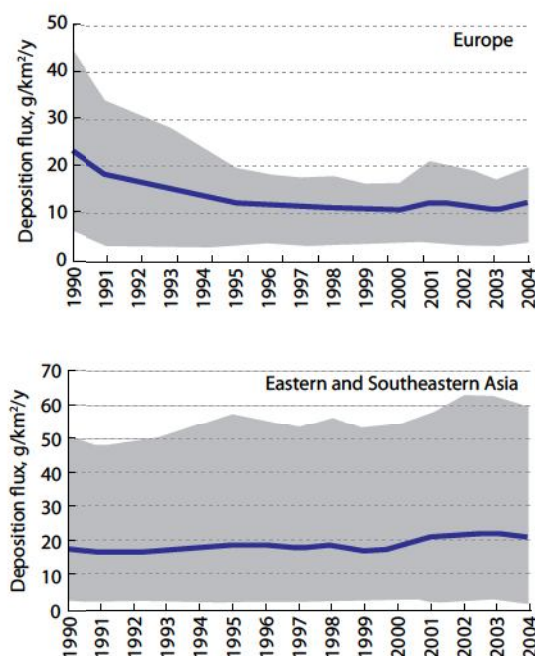
Longer-term trends, on the scale of centuries, have been done with box models. The amount of mercury in the atmosphere has increased by a factor of about three since the start of the industrial age. Mercury in the upper 100 meters of the ocean has increased by about 180%, but only by 11-17% in the deep oceans below 1500 meters. The difference between shallow and deep waters is the result of the enormous reservoir of mercury already present in pre-industrial oceans and the low rate of transfer of mercury from shallow to deep waters. A separate study showed that anthropogenic mercury may take decades or centuries to reach deep ocean waters. The oceans were found to play an important role in global mercury cycling.

A study of long-term trends in deposition using a geographical model found that deposition of mercury has doubled on a worldwide basis since the start of the industrial age (compared with a three-fold increase measured in soils and sediments, see Chapter 7), with a five-fold increase in major source regions. This same study found that, in the United States, 68% of deposition is from anthropogenic sources, with 20% from current North American sources, 31% from current sources in other regions, and 16% from re-emissions of historical anthropogenic mercury from soils and deep ocean water.

## Uncertainties in modelling

Models are simplifications of reality. As such, they inevitably err in some respects. Nonetheless, as the preceding sections have shown, modelling results can be useful, particularly in the absence of observational data. Improving models, however, requires recognition of their shortcomings and additional studies to provide better information on model inputs and the processes simulated in the models. Models also require accurate data to begin with, such as emissions data, the uncertainties of which were discussed earlier in this report. The models can be tested to some degree by comparison with observational data. Models are considered to be optimally configured when their results are consistent with observational data.

Quantitative estimates of uncertainty are typically made in separate studies, such as intercomparison studies. One of these studies concluded that the models can predict gaseous elemental mercury concentrations roughly within 30% of observations and wet deposition within a factor of two or so. On the other hand, dry deposition predicted by the



models varies by a factor of 10 due to the lack of observational data to constrain the models.

Model results require careful scrutiny, even when they match observational data. For example, a model might underestimate dry deposition, thus indicating more mercury available for wet deposition than is really the case. But if the model also underestimates the rate of wet deposition, it could still produce results that match observations of wet deposition. While model intercomparisons may identify research priorities like this, only further observational and experimental data will provide reliable answers.

Using models to establish source-receptor relationships or to predict the results of changes in emissions requires understanding the principles involved. Otherwise, a model that produces results that agree with today's observations may turn out to be flawed with regard to tomorrow's conditions. Among the priorities for further research are determining reaction rate constants, re-emission rates, and other parameters at the temperatures and other conditions found in the atmosphere rather than just in the laboratory. The exact compounds involved are also important, but at present are not known with any certainty. The absolute and relative concentration of reactive gaseous mercury is crucial to deposition, but cannot yet be measured on a regular basis in monitoring stations.

Uncertainties in the atmospheric chemistry of mercury are also a challenge. Transport of gaseous elemental mercury, for example, can be modelled

with the flow of air masses, but the oxidation of gaseous elemental mercury and its consequent deposition cannot be accurately modelled without better understanding of how those steps occur. If anything, reactive gaseous mercury and total particulate mercury present even greater challenges. This is especially problematic when trying to project into the future, particularly in light of climate change, which is expected to alter some of the basic conditions in which mercury reactions take place.

Additional uncertainty stems from the behaviour and reactions of mercury on the earth's surface. The ways in which oxidized mercury, once deposited, is converted back to elemental mercury and then re-emitted is not well understood, particularly for terrestrial systems, which involve both vegetation and soil. The re-emission of mercury is an essential component of mercury cycling, but the amount of mercury involved

is not clear. In areas with historically high uses of mercury, re-emission rates are expected to be higher, but the global ratio of re-emission from natural sources versus anthropogenic ones remains controversial. Capture of mercury in deep-ocean sediments is believed to be the main mechanism by which mercury is removed from global cycling, but ocean-atmosphere cycling is not captured in many models. Further research is needed on the reactions that occur in surface ocean waters, which govern how much mercury is re-emitted and how much is available for deposition into deep-ocean sediments. Ultimately, models aim to replicate how mercury travels from source to receptor and, after deposition, how it will enter and behave in the ecosystem. Today's models help show some important aspects of mercury cycling, but more remains to be done.