

EXECUTIVE SUMMARY

Working Group 37

Mercury in the Aquatic Environment: Sources, Releases, Transport and Monitoring

Authors

Principal authors:

Helen Keenan (Chairman)

Sornnarin Bangkedphol (Technical Secretary), Alo Babajide, Christine Davidson, Jean Guimeraes, Milena Horvat, James Hurley, Joy Leaner, Robert Mason, Apisit Songsasen, Tomiyasu Takashi, E.Vasileva-Veleva

Other contributors were:

Adeleke Adebayo, Antonia Bartzou, Antoine Assal, Derek Duncan, David Kocman, Ralph N McAleer, Nives Ogrinc, Keith Torrance, Dusan Zagar

Rationale for the report.

The establishment of a Working Group (WG) to address issues around the management of methyl mercury was proposed by the GESAMP Executive Committee in February 2006. The need for a new WG was related to the recent designation of methyl mercury as a Persistent Organic Pollutant as a candidate for inclusion in the Stockholm Convention, and the ensuing debate amongst the international scientific community. Discussion during the 34th Session of GESAMP in 2007 resulted in a revised focus (and revised Terms of Reference) for the WG to be an expanded review of mercury and its compounds (related to sources, transport and fate) and threats to the marine environment. Initially, UNIDO was the lead agency but withdrew their support due to changing policy priorities shortly before the 35th Session. This led to efforts to align the part-completed GESAMP study with the UNEP (Chemicals) Global Mercury Partnership, with a focus to provide a background report on mercury in the marine environment in support of the development of the UNEP Mercury (Minamata) Convention.

The preliminary report was completed in 2011 and submitted to UNEP. The original intention had been to publish the results of the study in the GESAMP Reports & Studies Series. It was decided not to pursue this option following the publication, in 2013, of the 'Global Mercury Assessment: sources, emissions, releases and environmental transport (GMA)' by UNEP. The GMA included significant contributions from the WG37 report.

Summary of the report

Introduction

Mercury (Hg) is a pollutant of global concern due to worldwide presence in all environmental compartments and potential to harm human health. It comes from natural and anthropogenic sources yet there are many factors about sources, pathways, and receptor linkages that are still not clearly understood.

Present in the earth's crust, Hg is naturally released into aquatic environments from transport and deposition of volatile mercury from volcanic sources and erosion of mercury-bearing rocks, especially from Hg mineral belts. Natural forest fires also contribute a significant amount of mercury, due to atmospheric deposition of Hg onto trees or uptake into trees if the area is high in Hg. It is not feasible to control and therefore to reduce the mercury from natural sources.

Mercury can anthropogenically be released from geologic stores by mining (coal or metals) producing Hg which may be used and recycled for a multitude of purposes. Once released, Hg will continue to cycle through soil, air and water. Airborne particles are deposited on land and water, with some being reemitted depending on local conditions (such as temperature). Human activity has increased mercury releases into the environment by tripling natural levels of emissions. The main anthropogenic atmospheric emissions come from fossil fuel combustion (ca 45% of total global emissions). The total of global anthropogenic emissions have been relatively stable over the last 15 years, with a shift in contribution from the western world to the eastern world. There has been a reduction in emissions from Europe and North America, reflecting the wider use of emissions' control technologies. However, the decreases have been offset by increases in South East Asia, notably China. Current Hg from anthropogenic activity is estimated to contribute approximately a third to a half of total global Hg emissions.

Particulate mercury and reactive gaseous mercury concentrations in the air depend on temperature, prevailing wind directions, local and regional sources, and *in situ* formation conditions in the atmosphere. Depending on the chemical form, some mercury is deposited within days while other forms are transported across hemispheres and may remain airborne for months or years. During circulation throughout the environment mercury can enter the aquatic environment through diffuse and point sources.

Atmospheric deposition (wet and dry) is the most common route of entry for Hg into remote water surfaces such as the Arctic and the Antarctic. The Hg load delivered to aquatic ecosystems associated with atmospheric deposition is approximately 7000 Tonnes per year. Mercury deposits into aquatic environments such as rivers, lakes, streams and estuaries are the major route of mercury transported into marine ecosystems. Wet deposition is the primary mechanism for transporting mercury from the atmosphere to surface water and land. Direct deposition into water, rather than air, is generally smaller in amount, but combined with atmospheric deposits to water, results in significant total Hg input to aquatic environments.

Chemical interactions

Once in aquatic systems, Hg can exist in dissolved or particulate forms and can undergo a number of chemical transformations. Some of this waterborne mercury may strongly bind with sediments. Contaminated sediments at the bottom of surface waters serve as mercury reservoirs, recycling Hg back into the aquatic ecosystem.

Mercury has a long retention time in sediments, so mercury that has accumulated in sediments may continue to be released to surface waters and other media for long periods (decades or longer).

Depending on conditions, mercury in water is readily converted to methylmercury by naturally present bacteria. Methylmercury (MeHg) is the most common form of organic mercury in the environment. Methylation occurs by biotic and abiotic processes, and transformation processes are influenced by several environmental factors such as pH, temperature, sulphate deposition, and availability of organic carbon. It is in this organic form that Hg mostly enters the food chain and bioaccumulates.

Methylmercury is more toxic when ingested, than elemental or inorganic mercury. MeHg magnifies up trophic levels causing top predators, including humans, to ingest potentially toxic doses. Ingestion of mercury-laden marine life is the major exposure route to humans. Humans that rely on diets based on seafood, biomagnify methylmercury within the body. High concentrations may trigger harm including negative neuro-developmental responses. Addressing releases of Hg into aquatic media is the current main cause for concern, because these releases place people all over the world - who consume predatory fish -at risk.

Sources

The main Hg releasing anthropogenic activities relate to energy, especially fossil fuel use and in particular coal; mining of metals (especially gold in artisanal mining), and some industrial processes such as the production of cement, chlorine, caustic soda and waste. These activities are grouped in these three main categories:

ENERGY

1. Combustion of fossil fuels
2. Extraction and processing of fossil fuels (particularly oil and gas)

PRODUCTION

3. Metal production
4. Mineral production
5. Industrial processes
6. Consumer products
7. Intentional product manufacture

WASTE

8. Recycled Metals
9. Waste incineration
10. Waste deposition
11. Human remains
12. Hotspots

To summarise diffuse mercury sources to aquatic systems:

- (1) Atmospheric deposition is the dominant input of Hg to the world oceans.
- (2) Riverine fluxes are a small part of the global budget.

(3) The majority of the Hg deposited to the oceans is re-emitted to the atmosphere as part of the Hg cycle. In contrast, only about half of the Hg deposited on land is re-emitted within similar timescales because Hg can associate strongly with soil.

(4) Deep sea burial is a relatively small component, which implies Hg is only removed from the global cycle via land sequestration on 'century' timescales; shallow burial may be re-released into marine food chains.

(5) Human activity has likely perturbed the natural cycle by increasing emissions to the atmosphere (and therefore to the land/water) by approximately a factor of three.

Point sources are the most direct entry routes to the aquatic environment. Effects may be severe locally but can also lead to long range transport. The most significant point sources are:

(1) Mercury mining and smelting: From a global perspective, most of identified mercury contaminated sites (> 70%) are concentrated in industrial regions of Europe and North America, and at the same time adjacent to the Atlantic Ocean and Mediterranean Sea. In other parts of the world, especially in Asia, the number and extent of mercury polluting sites are increasing, in contrast to Europe and North America. This is thought to be due to shifting manufacturing and the rising use of mercury in various processes, such as small scale gold mining, with Hg discharges directly to water.

(2) Industrial and urban sites including production of acetaldehyde, PVC/VCM, vinyl acetate and oil refineries; the Northern Hemisphere has the greatest concentration of these sites.

(3) Offshore industrial activities (oil and natural gas): All phases of production, processing and refining of oil and gas have mercury release potentials, depending on the mercury content of the original crude oil and gas. Crude oils from South America and Asia tend to have higher mercury contents than crude oils from the North Sea and most of North America (Texan oil is high in Hg).

(4) Direct Discharge from Waste Water Treatment Plants: Municipal plants focus domestic, industrial and commercial liquid wastes. The variability of influent concentrations can be very high due to industrial and domestic activity variations. Some countries have legislation regarding discharge but there are no global directives.

Production, use and disposal of over 3000 different types of mercury-containing products and wastes can result in the release of mercury to local aquatic systems. Indirect Hg pathways to waters occur via soil erosion and surface runoff. For mercury transportation by hydrological cycles, two separate environments and processes are considered, respectively:

(1) Catchment areas. The most important factors controlling mercury release by terrestrial erosion are meteorological conditions (e.g. storms).

(2) Contaminated coastal environments. Mercury released to the aquatic environment due to erosion ultimately ends up in seas and oceans, via riverine transport. Many contaminated sites are located at or near the coastline, including mercury containing product industries (e.g. >40% of all chlor-alkali plants) being

located at the coast. These sites have for decades introduced waste containing mercury directly into local estuaries. Multi-year accumulation of direct releases from industry, and contaminated sediments mean many coastal areas are considered contaminated with mercury. About 150-300 Tonnes of mercury are released annually to the global mercury budget from these mercury contaminated sites. Based on this, mercury from such contaminated sites contributes approximately 5% of the global anthropogenic atmospheric emissions every year. On average, more than 50% of these atmospheric emissions from contaminated sites originate from precious metal processing (large/small scale), followed by mercury mining, polluted industrial sites, non-ferrous metal processing and the chlor-alkali industry. The current estimates of mercury releases via rivers to estuaries due to soil erosion suggest that these releases are significant and are in the same order of magnitude as the atmospheric.

Control of releases

Consequently, reduction of mercury emissions reduces concentrations of the contaminant in air, and precipitation thus must be the dominant mechanism of control. Reduction of reliance on fossil fuels (particularly limiting coal burning) is most likely to reduce the amount of mercury in the global cycle. This would effectively reduce the amount of Hg deposited in aquatic environments, eventually reducing the potential for methylmercury bioaccumulation in species which are consumed by humans.

There are several types of controls and environmental quality standards that have been implemented in some countries, but many countries remain without controls. Global Environmental Quality Standards (EQS) specifying maximum acceptable mercury concentrations in fresh/marine waters and sediments are urgently required, particularly for aquatic environment. Although some (mostly developed) countries do have such standards there is a need for global values to be agreed and adopted.

Research

While it is difficult to truly “separate” anthropogenic from natural sources in samples, cumulative evidence allows for source attribution and hypotheses about important sites of Hg transformation and bioaccumulation. Emerging technologies for atmospheric Hg speciation and Hg analyses, (e.g. by plotting isotopic ratios) show great promise, but are subject to interpretations based on limits of knowledge of Hg transformation and fractionation. Addressing the current mercury contamination in the aquatic environment heavily relies on understanding site specific conditions, and on watershed and catchment management strategies to allow development of best management practices necessary to protect the aquatic environment.

Sedimentary records provide insight by reconstructing historical Hg deposition in environmental settings, including lakes, peat bogs and depositional zones of oceans and glaciers. Longer term cores (> several hundred years) give more accurate estimates of true background Hg levels prior to anthropogenic influences. The key to interpreting deposit patterns is to acquire supplementary information from sampling, to strengthen conclusions.

Mercury is found throughout the ecosystem as divalent inorganic mercury (Hg^{2+}) in natural waters, metallic form (Hg^0) in the atmosphere, and monomethylmercury (CH_3Hg^+) in water or sediments. There is great need for analysis and analytical techniques which are able to distinguish different mercury species. In order to effectively monitor and collate data, analytical methods must be accurate, verifiable and reproducible. There are many approved methods for the analytical measurement

of methyl- and total mercury recognised by authorities such as the US Environmental Protection Agency, but emerging speciation methods are still experimental and standardised methods are required for a better understanding of source apportionment. More resources are required to support studies using newer techniques to validate methods and to assess if controls from anthropogenic sources and legislative measures are effective.

The current methods require proper quality assurance and control (for example using certified reference materials). There is need for proper training in sampling, sample preparation and analysis so that data generated is accurate and that valuable resources are spent generating data that is fit for purpose. Many studies have failed to ensure correct procedures and therefore results are unconvincing and difficult to compare with other researchers' results.

Methylmercury appears to be accumulating in various species, detrimental to health, and potentially harmful to top predators such as ocean mammals, bears and humans. Although there are many programs that measure concentrations of Hg in various species on various levels in the food chain in the aquatic environment, there is currently no single global approach. Most research is from the Northern hemisphere. Southern hemisphere data is less well represented; the amount of Hg released and the potential impacts of Hg in the Southern Hemisphere are therefore likely to be underestimated.

Real-time monitoring and marine cycling research studies are continually emerging, better defining sources and fate of Hg. As oceans are currently the main area where further Hg studies are required, there is a vital requirement for a global marine monitoring program, monitoring marine mercury distributions and speciation data in order to fully comprehend past and present dynamics of mercury in the marine environment.

Monitoring

Methyl and total mercury concentrations form the basis of many monitoring programmes, necessary to evaluate the potential adverse physiological impacts of mercury in the environment on different species, including humans. The regions that currently monitor mercury in fish and marine mammals are:

- Arctic Region
- Antarctic Region
- Baltic Sea
- Caspian Sea
- North East Atlantic

Various “mercury monitoring engagement” organisations and treaties continue to further country-specific investigation of fish and marine mammals containing mercury. Some of these regions and organizations, respectively, are:

- Arctic: Arctic Monitoring and Assessment Programme (AMAP)
- Baltic: Helsinki Commission (HELCOM)
- Black Sea: The Commission on the Protection of the Black Sea against Pollution
- Eastern Africa: UNEP (United Nations Environment Programme) Action Plan for the protection, management and development of the marine and coastal environment of the Eastern African region & Nairobi Convention (Nairobi Convention

for the Protection, Management and Development of the Marine and Coastal Environment of the Eastern African Region), FAO (Food & Agriculture Organization) & WHO (World Health Organization)

- East Asian Sea: COBSEA (Coordinating Body on the Seas of East Asia)
- Mediterranean: Mediterranean Action Plan
- North-East Atlantic: OSPAR Commission (The Oslo and Paris Commissions)
- North-West Pacific: NOWPAP (The Northwest Pacific Action Plan)
- South Asian Seas: SACEP- South Asia Co-operative Environment Programme
- South East Pacific-SPREP-South Pacific Regional Environmental Programme
- West and Central Africa: Regional Seas Programme
- Wider Caribbean: UNEP Caribbean Environmental Programme

Monitoring data can be assessed in terms of model applicability on the basis of various features, such as:

- Spatial trends
- Temporal trends (annual, seasonal, and diurnal)
- Speciation features (physical/chemical state)
- Absolute concentration levels
- Multimedia features (POPs-persistent organic pollutants and Hg)

Variations in aquatic characteristics across ecosystems thus far reveal no distinct spatial patterns. This challenge, combined with long range transport of atmospheric emissions, means it is not feasible to pick and choose where to reduce mercury pollution in order to achieve safe aquatic mercury targets. Rather, a global approach where reductions take place at all facilities around the world is more likely to achieve results.

Monitoring programs enable accurate assessment of environmental responses to mercury emission alteration and reduction. The following tables offer suggestions as to the variety of monitoring data required for accurate analyses of changes in mercury loading. This may also enable measurements of how efficient future reduction strategies will be.

Table 1. Long term monitoring strategies

	Measurement	Frequency
1.	Wet atmospheric deposition	Weekly
2.	Surface soil sampling	Twice per year
3.	Surface water sampling	Twice per year
4.	Young fish mercury sampling	Twice per year
5.	Piscivorous (fish eating) species sampling	Annually
6.	Wildlife sampling	Annually

Table 2. Intensive monitoring strategies

	Measurement	Frequency
1.	Atmospheric mercury by species	Continuously
2.	Mercury evasion	Monthly
3.	Watershed yield from surface and groundwater	Monthly

4.	Long-term sediment depth mercury profiles	3-5 years
5.	Mercury and methylmercury in water columns	Twice per year
6.	Phytoplankton and algae mercury levels	Monthly
7.	Zooplankton and benthic invertebrate sampling	Monthly

Such programs are unlikely to be adopted voluntarily and universally due to lack of resources, facilities and trained analysts (particularly for developing countries). Therefore, apart from the new convention, the ability to comply, and the capacity to prove compliance, has to be recognised and supported.