ScienceDirect

Journals & Books

? Robert Mason

≡   📄 **Download**   **Share**   **Export**

Geochemistry of Mercury in the Marine Environment

Zofia Baumann ✉, Sofi Jonsson ✉, Robert P. Mason ✉

⊞ **Show more**

Get rights and content

Abstract

Anthropogenic inputs, predominantly from the atmosphere, have increased the concentration of mercury (Hg) in the upper ocean and the levels in marine organisms. The biogeochemical cycling of Hg in the ocean is complex as it can be transformed by both abiotic and biotic processes into methylated Hg (mono- (MMeHg) and dimethylmercury (DMeHg)) and reduced to volatile elemental Hg (Hg(0)). Methylation and demethylation occur within the marine ecosystem and the net formation of MMeHg leads to its bioaccumulation in the marine food web. Levels of MMeHg in apex species are high enough to affect human and wildlife health.

Keywords

Atmospheric deposition; Bioaccumulation; Biogeochemistry; Demethylation; Dimethylmercury; Exposure; Gas exchange; Human health; Mercury; Methylation; Methylmercury; Ocean; Redox chemistry; Trophic transfer

Nomenclature

Hg

  Mercury

MMeHg

  Monomethylmercury

DMeHg

  Dimethylmercury

Hg(0)

  Elemental mercury

Hg(II)

  Ionic mercury

hgcAB

  Mercury methylating genes

HgS

  Solid mercury sulfide (cinnabar)

Introduction

Mercury (Hg) is one of a few metals that have been added to the ocean in sufficient quantity from anthropogenic activities to measurably alter its upper ocean preanthropogenic concentration. These increases over time have now been documented based on sediment core analyses, and validated by global Hg model simulations (Fig. 1) (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018). Currently, Hg is released into the environment primarily as a result of human activities, with a small fraction from terrestrial natural sources, such as volcanoes and rock weathering. There are several chemical forms of Hg that are present in nature. One of these is elemental Hg (Hg(0)), which occurs predominantly as a gas in air, water, terrestrial soils and aquatic sediments. Hg(0) is produced via the reduction of ionic Hg (Hg(II)), and as Hg(0) can be oxidized to Hg(II) in the surface biosphere; there is an active recycling between these forms. Being volatile, Hg(0) can readily exchange between these surface reservoirs, thereby prolonging the residence time of Hg in the biosphere (Amos et al., 2015). Whereas the formation of Hg(0) in the ocean and terrestrial environment involves natural processes (microbial and photochemical

transformations), much of the Hg(II) being transformed was originally emitted to the biosphere from anthropogenic sources. These inputs predominantly consist of recycled anthropogenic Hg, and not Hg naturally occurring in the earth's surface layers (Fig. 1) (AMAP/UNEP, 2018). Overall, the magnitude of the exchange of Hg(0) between the atmosphere, ocean and terrestrial landscapes is significant in the global Hg cycle. Atmospheric processes lead to the transport of Hg, both as Hg(0) and Hg(II), and influence the rate of transformation, and their deposition onto land and ocean. While Hg recycling is active in the terrestrial, freshwater and marine biospheres, it is eventually removed from these systems through burial in coastal and deep ocean sediments, lake sediments, and subsurface soils (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018).
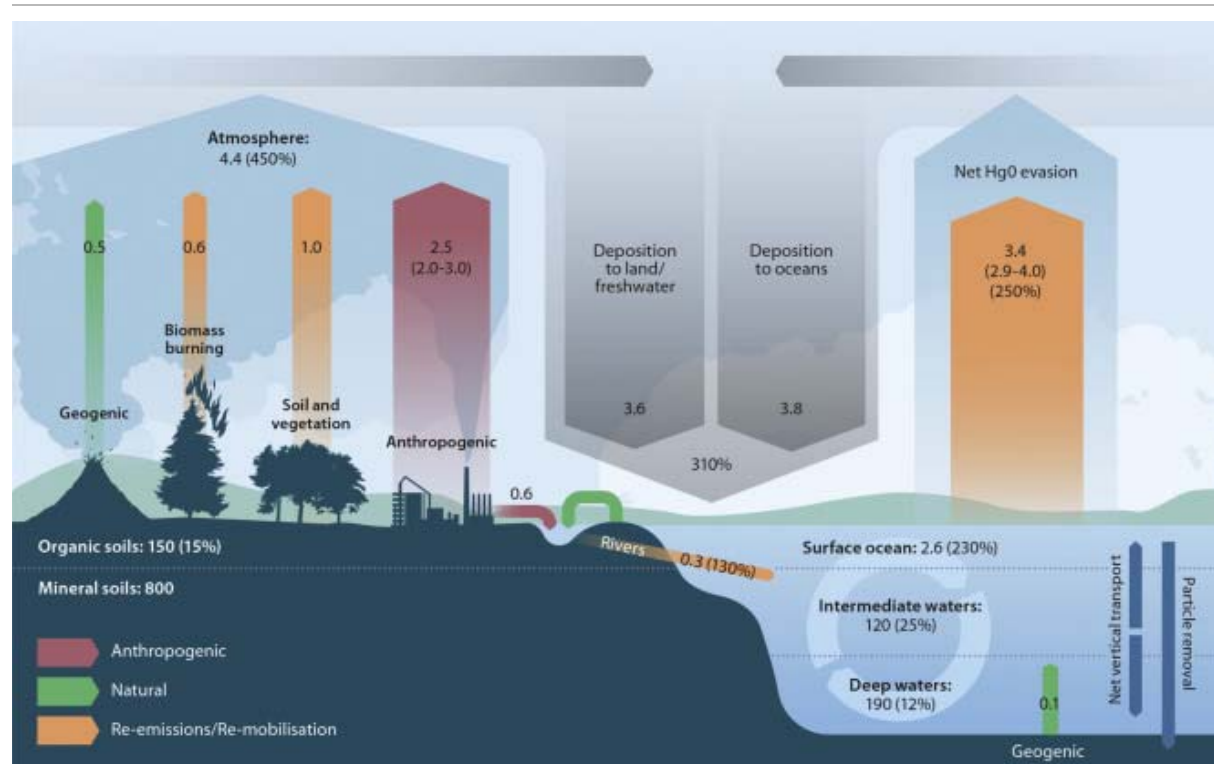
Download full-size image

Fig. 1. Global mercury cycle highlighting the major fluxes between the ocean and other reservoirs, and within the ocean itself. Arrows represent the estimate fluxes in metric kilotons/year (kt/yr) between reservoirs with the estimated percentage increase in the flux due to anthropogenic releases of mercury given in brackets for each flux. For fluxes with high uncertainty, a range of values is also given. Values within each reservoir (in kt) indicate the inventory of mercury within the reservoir, with the predicted increase again shown in brackets.

Figure taken from AMAP/UNEP 2018 (reference AMAP/UNEP (2018). Technical background report for the global mercury assessment; http://www.mercuryconvention.org/Resources/Information/Publications/tabid/3429/lar US/Default.aspx (in press)) and used with permission.

Aside from the inorganic forms of Hg that exist in the environment, organic forms, predominantly monomethyl- (MMeHg) and dimethylmercury (DMeHg), are of high significance due to their bioaccumulative (i.e., MMeHg) and toxic properties (Eagle-Smith et al., 2018). While MMeHg represents a small fraction of the total Hg in the ocean, it is the Hg form of primary concern for human and wildlife exposure, as it is toxic and bioaccumulates most efficiently in food webs (Eagle-Smith et al., 2018; Lee and Fisher, 2016). While MMeHg is produced from Hg(II) mainly in aquatic ecosystems through microbial processes (see below), it can be transformed into DMeHg, or back to Hg(II) (Driscoll et al., 2013; AMAP/UNEP, 2018). The present thinking is that in the ocean, much of the MMeHg is formed within the water column in regions of enhanced microbial activity, while MMeHg production and flux out of sediments contribute to the overall MMeHg pool in shallow ecosystems (Obrist et al., 2018; AMAP/UNEP, 2018). Therefore the pathway for the uptake and trophic transfer of MMeHg depends on the specific location within the ocean. Ecological factors such as the complexity of the food web, as well as abiotic and biotic processes controlling the bioavailability of MMeHg to phytoplankton, control bioaccumulation in marine food webs. Overall, both forms of methylated Hg are relatively unstable within the water column and sediments, thus their presence throughout the ocean, indicates the continual production of methylated Hg within the ocean (Driscoll et al., 2013; Obrist et al., 2018; AMAP/UNEP, 2018).

Consumption of seafood and freshwater fish with elevated levels of MMeHg is the primary driver of public health concerns related to Hg (Eagle-Smith et al., 2018). The largest bioaccumulation step is between water and unicellular planktonic organisms (Lee and Fisher, 2016). Therefore, information on Hg levels in organisms at the base of food web, and the controlling factors, is important for our ability to predict concentrations in the upper trophic levels, that is, fish, marine mammals and birds (Eagle-Smith et al., 2018; Schartup et al., 2017). Moreover, understanding of bioaccumulation at lower food web levels enables tracking changes that occur on relatively short time scales, that is, weeks to ~ 2 years, representing life span of diverse invertebrate species. This is important, as there are now global efforts to reduce Hg inputs, that is, the Minamata Convention on Mercury, which can trigger local policies to decrease Hg emissions to the atmosphere and hence reduce its influx into surface ocean waters (AMAP/UNEP, 2018).

Sources and Sinks of Mercury in the Ocean

The estimates of the sources to and sinks of Hg from the ocean, outlined in Fig. 1, and the percentage by which each flux and reservoir of Hg has been impacted as a result of anthropogenic Hg inputs are compiled using recent literature (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018). It has been estimated that the concentration of Hg in the atmosphere and its atmospheric fluxes have changed the most as a result of human activity as it receives Hg directly from anthropogenic sources and because of the rapid exchange of Hg between the atmosphere and surface reservoirs (Fig. 1). Conversely, given the large volume, isolation from anthropogenic sources and slow mixing of the deep ocean, the concentration of Hg in that part of the ocean has changed the least over the anthropogenic period. This conclusion is primarily based on modeling results as preindustrial concentrations of Hg in seawater cannot be accurately reconstructed due to the lack of reliable proxies. Changes in the ocean mixed layer Hg concentration tracks the atmosphere more closely given the rapid cycling and mixing of these two reservoirs (Fig. 1). The upper ocean is the region where much of the biological activity occurs, and methylation of Hg within the sub-thermocline waters is hypothesized as an important source for MMeHg to the surface ocean (Obrist et al., 2018; AMAP/UNEP, 2018). It is transported to the surface ocean layer by mixing and advection.

The Hg input to the ocean is primarily through atmospheric deposition, whether via precipitation, or dry deposition of gaseous and aerosol Hg phases. These Hg inputs predominantly consist of Hg(II). Loss of Hg from the ocean via evasion of Hg(0) gas is the dominant sink (Fig. 1) (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018). In the surface ocean, Hg(II) reduction and Hg(0) oxidation reactions are mediated by light (i.e., photochemically) or by microorganisms. These transformations lead to the buildup of Hg(0) in the ocean mixed layer to supersaturated levels, consequently driving its loss to the atmosphere via evasion of Hg(0) (Obrist et al., 2018; AMAP/UNEP, 2018). Much of the Hg transported to the ocean via rivers is buried and removed within coastal waters and the input to the open ocean is a small fraction of the riverine flux (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018). This is primarily because Hg is highly particle-reactive and either taken up into biota or detrital particles in rivers and coastal waters, and is efficiently removed from the water column with particles through coagulation and sedimentation (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018).

The distribution of Hg in its various forms throughout the ocean depends on the processes controlling its formation and degradation, and the rate of these processes in a

specific location. As an example of the distribution of inorganic and organic Hg, the data derived from the US GEOTRACES cruise in the North Atlantic in 2010/11 is shown in Fig. 2 (Bowman et al., 2015). Overall, concentrations of total filterable Hg in the water (diss. THg, obtained by filtration with 0.45 µm pore diameter filter) are low in surface waters as it is actively scavenged by particles. Concentrations of diss. THg are higher in intermediate waters characterized by lower levels of oxygen due to active remineralization of biogenic particles. As evident in Fig. 2A, higher diss. THg concentrations are also seen in the vicinity of the mid-Atlantic ridge, with hydrothermal vents being the presumable source. However, the importance of hydrothermal inputs as a source of Hg to the global ocean is debated given that a hydrothermal signal has not been found consistently in the vicinity of diverse vents in different ocean regions, and as data are limited (Obrist et al., 2018; AMAP/UNEP, 2018). For MMeHg, its dissolved concentrations are higher in the intermediate waters and in the deeper waters, and are low in the surface waters (Fig. 2B) (Bowman et al., 2015). Such patterns are driven by microbial uptake and degradation of MMeHg throughout the water column. Additionally, diss. MMeHg is photochemically degraded in surface waters, primarily by UV radiation (Obrist et al., 2018; AMAP/UNEP, 2018).
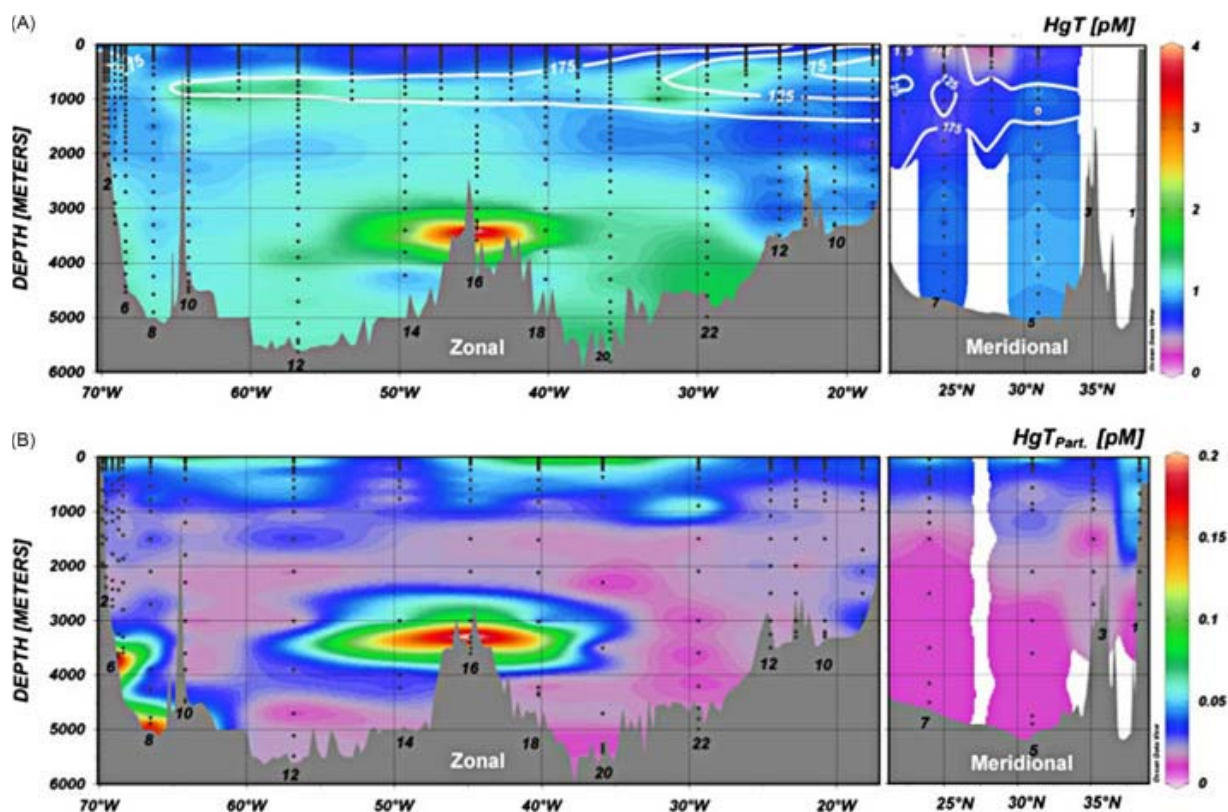
Download full-size image

Fig. 2. Distributions of total dissolved mercury (HgT) and monomethylmercury (MMHg in the figure) throughout the water column of the ocean for samples collected during the US GEOTRACES cruise in the North Atlantic in 2010/11 (there were two cruises). The data are shown as two sections: (1) the zonal section is from Woods Hole, MA, USA to the Cape Verde Islands; and (2) the meridional section from there to Portugal. Concentrations are in molar units (1 pM = 0.2 ng/L) and dots on the plot represent the locations of the samples analyzed. Distributions between points are interpolated using Ocean Data View.

Figure from Bowman, K. L., Hammerschmidt, C. R., Lamborg, C. H., Swarr, G. (2015). Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections. *Deep-Sea Research Part II* **116**, 251–261 and used with permission.

Overall, based on current understanding (Driscoll et al., 2013; Amos et al., 2015; Obrist et al., 2018; AMAP/UNEP, 2018), the distribution of inorganic Hg and methylated Hg in the ocean is largely driven by: (1) current anthropogenic inputs, which are dominated by coal burning and artisanal gold mining activities (Obrist et al., 2018; AMAP/UNEP, 2018), and prior releases (Amos et al., 2015), for example, currently, decreasing atmospheric emissions in North America and Europe and increasing emissions in Asia and in developing nations since the early 1990s; (2) primary productivity and other microbial processes in the region, for example, the rate of organic matter degradation; (3) the atmospheric and riverine external inputs; and (4) climate change. The impact of climate change is large but little studied. For example, changing climate influences the duration of sea ice cover and productivity in polar regions, and hence Hg and MMeHg cycles (Obrist et al., 2018).

Methylation of Inorganic Mercury and Demethylation of Methylated Mercury

In the past, MMeHg was released into the environment from anthropogenic sources when used as a fungicide or as industrial waste (Hsu-Kim et al., 2018). Other organic mercury compounds were also used for various applications (Mason, 2015). This resulted in a number of poisoning catastrophes in the 1950–70s, and ultimately in the enactment of regulations to eliminate the use and emission of MMeHg and other Hg compounds (Hsu-Kim et al., 2018). At that time, these events were the main driver for acknowledging Hg as a serious environmental contaminant. On a global scale, however, anthropogenic sources of MMeHg have had limited impact on the concentrations of

MMeHg in marine ecosystems. Instead, MMeHg in the marine ecosystems is formed from Hg(II) of natural and anthropogenic origins, predominantly by microbes (Hsu-Kim et al., 2018; Mason, 2015).

Biotic Methylation of Mercury

In 1969, Jensen and Jarnelov discovered that inorganic Hg could be methylated in the environment to MMeHg and DMeHg (Mason, 2015). These transformations were suggested to occur via biotic processes. Several bacterial strains of sulfur and iron reducing bacteria, methanogenic archea, and bacteria from the phylum Firmicutes have since been identified as "Hg methylators" (i.e., having the ability to convert inorganic Hg to MMeHg) (Mason, 2015; Podar et al., 2014). The biochemical pathway of this transformation was unclear until 2013, when Parks et al. (Parks et al., 2013) identified two genes, hgcA and hgcB, whose presence in Desulfovibrio desulfuricans were required for methylation of Hg(II). Hence, microorganisms equipped with this gene pair are now referred to as Hg methylators, while those with their absence as known nonmethylators. The depletion of one or both of the genes from D. desulfuricans and Geobacter sulfurreducens (known Hg methylators) confirmed the necessity of both hgcAB genes. This new scientific advance has enabled researchers to now pursue searches of new, previously unknown Hg methylators among diverse microbes in various environments (Hsu-Kim et al., 2018; Mason, 2015; Podar et al., 2014; Parks et al., 2013).

Anoxic conditions were initially assumed necessary for substantial methylation of Hg to occur as microorganisms that were known to mediate this transformation were strictly anaerobic. Most of our knowledge on Hg methylation has therefore been derived from studies focusing on systems such as anoxic freshwater and marine sediments and terrestrial soils. However, sources of methylated Hg remain poorly understood in ocean water (Obrist et al., 2018; AMAP/UNEP, 2018; Hsu-Kim et al., 2018). In coastal zones, MMeHg in the water can originate from terrestrial runoff, input from offshore water masses due to tidal exchange, and fluxes from sediments (e.g., diffusion of dissolved MMeHg from pore water to the overlying water, and exchange between water and particles during sediment resuspension) (Driscoll et al., 2013; AMAP/UNEP, 2018; Hsu-Kim et al., 2018). As previously described, inputs of MMeHg are however often insufficient to account for observed concentrations of MMeHg in the pelagic zone of the open ocean. Methylation of Hg in the water column is therefore hypothesized to be of importance for deeper coastal, as well as offshore oceanic ecosystems (Obrist et al., 2018; AMAP/UNEP, 2018; Hsu-Kim et al., 2018). In situ methylation of Hg in marine waters is also supported by experimental studies (e.g. the Mediterranean Sea and the

Canadian Arctic Archipelago) (Hsu-Kim et al., 2018). Depth profiles across marine systems consistently show increased MMeHg concentrations in the subthermocline oxygen minimum zone (Obrist et al., 2018; AMAP/UNEP, 2018; Bowman et al., 2015; Hsu-Kim et al., 2018) suggesting that Hg methylation in marine systems could be driven by microbial processes related to the remineralization of settling organic matter, as release of MMeHg from remineralization of the settling particles cannot account for the concentration increases (Driscoll et al., 2013; AMAP/UNEP, 2018). Anoxic niches in marine particle aggregates could facilitate Hg methylation by anaerobic microorganisms and the potential for this pathway has been demonstrated in the laboratory (Mason, 2015).

In the search for potential Hg methylators in marine systems, Podar et al. (Podar et al., 2014) investigated the occurrence of the *hgcAB* genes in existing metagenomic data from marine waters and sediments. While the DNA sequences similar to those present in the previously described *hgcAB* genes were commonly identified in marine sediments, they were only detected in 5% of the water samples, and not in surface waters. Moreover, these sequences did not match any known methylators that have been possible to culture under laboratory conditions. This is not surprising given that < 1% of marine bacteria can be cultured. It is also reasonable to speculate that most bacteria methylating Hg in the environment have not been identified and that additional biotic methylation pathways could exist.

Bacterial methylation of Hg under sulfidic conditions, such as in reducing sediments and soils, is also controlled by the chemical speciation of Hg in both the solid and dissolved phase (Hsu-Kim et al., 2018; Mason, 2015; Jonsson et al., 2014). Early work suggested Hg methylating bacteria in anoxic environments acquired dissolved neutral Hg–S complexes via passive diffusion. More recently, uptake of dissolved low molecular weight thiol–Hg complexes via active transport (thiols are organic compounds containing reduced sulfur groups which strongly bind Hg) have been demonstrated as a viable pathway (Mason, 2015). Precipitation of inorganic Hg with sulfide and adsorption of Hg to organic matter limits the availability of Hg for methylation in sediments and soils. The degree to which the chemical speciation of inorganic Hg in marine waters controls Hg methylation remains to be elucidated (AMAP/UNEP, 2018). In marine waters, with low dissolved organic carbon (DOC) content and sulfide, inorganic and organic Hg sulfide complexes are not likely to be abundant. Instead, Hg is complexed to a greater degree by chloride at low DOC, and occurs mainly as $HgCl_4^{2-}$ (aq) with a small fraction as neutrally-charged $HgCl_2$. Recent work has suggested that charged chloride complexes could be taken up by bacterial cells although only under anoxic

conditions (Stenzler et al., 2017). As inorganic Hg in marine waters mainly occurs in the form of dissolved inorganic and organic complexes, precipitation and adsorption of Hg to particles are likely less important processes in controlling the methylation of Hg than processes in sediments and soils. The origin of organic matter also appears as an important factor in controlling Hg methylation, for example, terrestrial organic matter appears to limit Hg methylation in coastal ecosystems (AMAP/UNEP, 2018; Hsu-Kim et al., 2018; Jonsson et al., 2014).

Abiotic Methylation of Mercury

In addition to microbial methylation, controlled experimentation has demonstrated the possibility of Hg methylation via abiotic pathways (AMAP/UNEP, 2018; Mason, 2015). Compounds confirmed to support the methylation of Hg(II) include humic materials, acetate, methylcobalamin and other methyl cobalt compounds, and methyl tin compounds. Elemental Hg, but not Hg(II), can be also methylated by methyl iodide. Conditions in the laboratory differ from the natural environment, hence the importance of abiotic methylation of Hg in marine systems remains uncertain. However, it is known that compounds such as methylcobalamin and methyl iodide can be bacterially produced. Therefore, zones of enhanced microbial activity could contribute to ex vivo MMeHg production via an abiotic pathway.

Demethylation of Monomethylmercury

As MMeHg, which has been formed in marine waters is readily degraded via both biotic and abiotic processes, it is not likely to be transported over long distances (AMAP/UNEP, 2018). Photochemical degradation is the main abiotic degradation pathway in surface sunlit waters. Both ultraviolet and visual light can degrade MMeHg directly through direct decomposition or indirectly through reactions with photochemically-produced reactive compounds (e.g., reactive oxygen species). Higher photochemical degradation rates are expected in open ocean waters compared to estuarine systems due to deeper penetration of both UV and VIS light in these locations. Monomethylmercury can be also degraded by bacteria (AMAP/UNEP, 2018; Mason, 2015). The two proposed pathways for bacterial degradation of MMeHg are the oxidative and the reductive pathway. Reductive degradation of Hg is carried out by bacteria carrying the mer operon resulting in methane (CH_4) as the final carbon product (Mason, 2015). The transcription of this operon is triggered at Hg concentrations expected in contaminated sediment and soils but not at the concentrations expected in marine waters (Podar et al., 2014). Mechanistic understanding of the suggested oxidative

reduction pathway, with carbon dioxide (CO_2) as the main carbon end product, remains unknown. This degradation could potentially be abiotic, involving the conversion of MMeHg to DMeHg and HgS in the presence of dissolved sulfide, organic ligands or sulfide surfaces (Jonsson et al., 2016; Charlotte et al., 2018).

Formation and Degradation of Dimethylmercury

A characteristic feature of marine systems, in comparison to the more studied terrestrial and freshwater systems, is the prevalence of DMeHg (AMAP/UNEP, 2018; Hsu-Kim et al., 2018; Mason, 2015). Dimethylmercury is not expected to bioaccumulate or to occur in concentrations of concern for human or wildlife health. However, DMeHg represents roughly half of the methylated pool of Hg in ocean water and degradation of DMeHg is hypothesized to be an important source for MMeHg (Driscoll et al., 2013; AMAP/UNEP, 2018; Hsu-Kim et al., 2018). How DMeHg forms and degrades in marine systems is however unknown. The vertical concentration profiles of DMeHg in seawater often match the profile of MMeHg (e.g., Fig. 2). It has thus been suggested that they are formed via the same processes or that the two methylated forms are in dynamic equilibrium. While early work suggested biotic formation of DMeHg directly from inorganic Hg, recent studies however suggest an alternative pathway, that is, formation of DMeHg from MMeHg (AMAP/UNEP, 2018; Mason, 2015; Charlotte et al., 2018). The extent to which DMeHg degrades in marine waters is also not well known. In the past DMeHg was thought to readily degrade in marine waters, especially in the presence of sunlight, but more recent studies have provided conflicting results suggesting higher stability (Driscoll et al., 2013; Mason, 2015).

Bioaccumulation of Monomethylmercury

As pointed out previously, MMeHg is the form of Hg that bioaccumulates most efficiently in marine organisms. Additionally, due to its toxicity, it is the primary Hg form of concern for human and wildlife health (Eagle-Smith et al., 2018; Hsu-Kim et al., 2018). The available pool of MMeHg for uptake in seawater is one of the key determinants of concentrations in marine organisms. Dissolved MMeHg (i.e., MMeHg in filtered seawater) occurs at extremely low concentrations (fM), yet its concentration in marine apex predators, for example, piscivorous fish, marine mammals and seabirds, can be up to eight orders of magnitude higher (AMAP/UNEP, 2018; Eagle-Smith et al., 2018). Overall, uptake of MMeHg by unicellular planktonic organisms is the key processes that transfers MMeHg from seawater into biomass, that is, marine organisms (Eagle-Smith et al., 2018; Lee and Fisher, 2016). Uptake by unicellular organisms and

assimilation across the gut membranes in metazoans is highly efficient, while in both groups of organism's removal of assimilated MMeHg is slow, resulting in its build up over time (Eagle-Smith et al., 2018; Lee and Fisher, 2016; Lee and Fisher, 2017).

Uptake of Monomethylmercury at the Base of the Food Web

The uptake of MMeHg into unicellular organisms serves as an entry point of MMeHg to pelagic food webs (AMAP/UNEP, 2018; Lee and Fisher, 2016; Charlotte et al., 2018). Experimental studies, using radioactive and stable isotopes of MMeHg as tracers, have demonstrated its high efficiency of incorporation into phytoplankton, resulting in volume concentration factors of up to six orders of magnitude. In metazoans, MMeHg is sourced nearly entirely from diet (AMAP/UNEP, 2018; Eagle-Smith et al., 2018; Lee and Fisher, 2016; Schartup et al., 2017; Lee and Fisher, 2017). Transfer of MMeHg between consecutive trophic levels is efficient, however trophic transfer factors (TFF = predator MMeHg/prey MMeHg) in higher trophic levels are never more than an order of magnitude (AMAP/UNEP, 2018; Eagle-Smith et al., 2018). Uptake of MMeHg from seawater into phytoplankton is therefore not only the entry point to food web, but also the most significant bioconcentration step of MMeHg considering the whole food web.

Diverse factors drive MMeHg concentrations at the bottom of the marine pelagic food web. Aside from the pool of available MMeHg, cell size appears as the most significant factor (Lee and Fisher, 2016; Schartup et al., 2017; Gosnell et al., 2017). In particular, the ratio of cell surface to volume drives the higher uptake of MMeHg into small phytoplankton, for example, cyanobacteria, in comparison to larger cells, for example, diatoms or coccolithophores. Because different taxonomic groups and species of phytoplankton display substantially different cell sizes, levels of MMeHg likely vary among them. To characterize levels of MMeHg bioaccumulation, at the base of the food web, scientists approximate different groups of plankton based on their size, separating them by size-dependent sequential filtration techniques. Concentrations of MMeHg in these pooled particles can be used as proxies for the corresponding size fractions of zooplankton, phytoplankton and bacterioplankton (AMAP/UNEP, 2018; Lee and Fisher, 2016; Schartup et al., 2017). Overall, experimental study has demonstrated differences in concentration factors among taxonomic groups of phytoplankton that correspond principally to cell surface area/volume ratios (Lee and Fisher, 2016).

Addition of nutrients to coastal marine ecosystems has caused local eutrophication, and a hypothetical agent of lowered MMeHg concentrations in zooplankton and fish due to

biological dilution (AMAP/UNEP, 2018; Eagle-Smith et al., 2018; Hsu-Kim et al., 2018). Such dilution of Hg in the biomass of an organism would occur if the rate of biomass increase would outpace the accumulation of MMeHg. Biological dilution of MMeHg has been demonstrated in freshwater zooplankton, and similar findings have been confirmed in the marine realm during the last decade (Fig. 3A) (Lee and Fisher, 2016; Gosnell et al., 2017). These results are also validated by computer modeling (Fig. 3B) (Schartup et al., 2017). Moreover, emerging studies are reporting the MMeHg and THg concentrations for specific zooplankton species (Schartup et al., 2017). Isolation of single zooplankton species showed that body size, as well as feeding habits and life history, are strong factors influencing MMeHg body burdens (Lee and Fisher, 2016; Lee and Fisher, 2017).
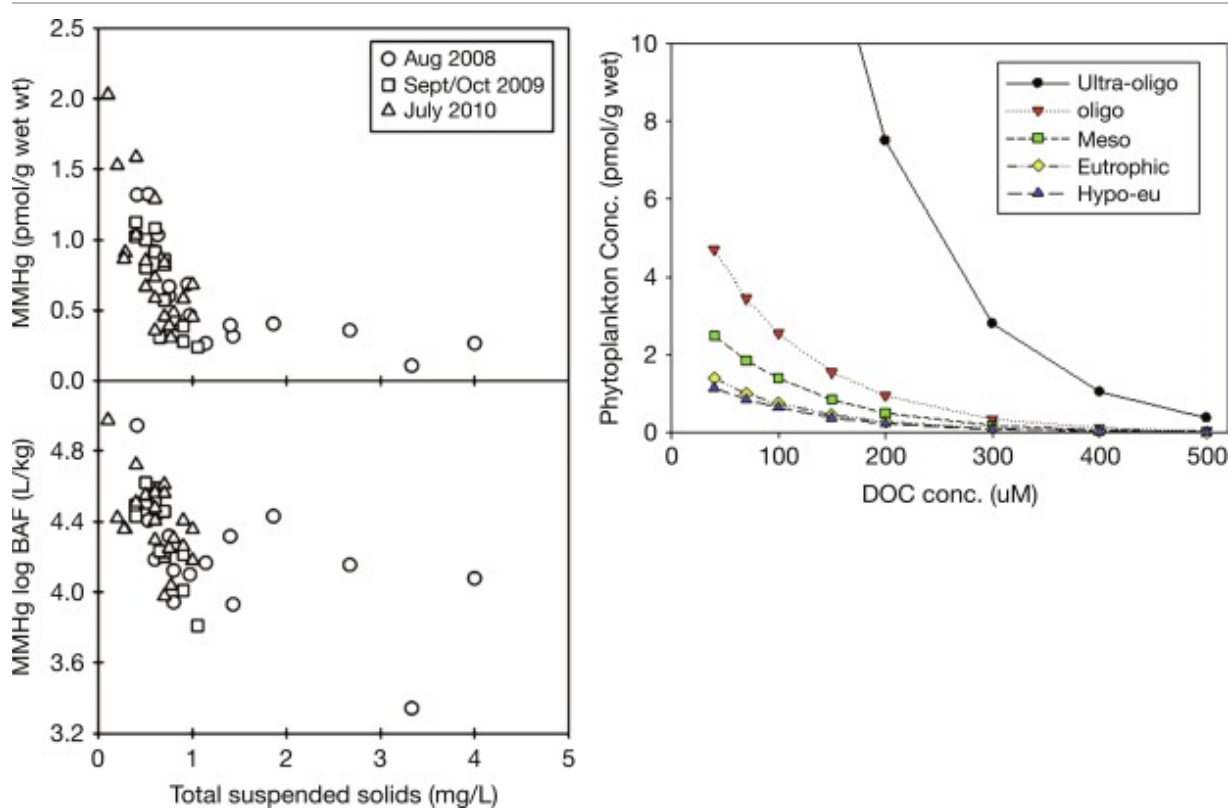
Download full-size image

Fig. 3. (A) Concentrations of methylmercury (MMHg in figure) and bioaccumulation factors (BAF; mass basis) of monomethylmercury (MMeHg) in microseston as a function of total suspended solids in surface (< 60 m) North Atlantic Ocean; and (B) modeled phytoplankton concentrations for MMeHg across concentrations of DOC and for different levels of eutrophication using the Schartup et al. (2018) model.

(A) Reprinted with permission from Hammerschmidt, C. R., Finiguerra, M. B., Weller, R. L., Fitzgerald, W. F. (2013). Methylmercury accumulation in plankton on the continental margin of the northwest Atlantic Ocean. *Environmental Science & Technology* **47**, 3671–3677, https://doi.org/10.1021/es3048619; (B) created using information in Schartup, A. T., Qureshi, A., Dassuncao, C., Thackray, C. P., Harding, C., Sunderland, E. M. (2017). A model for methylmercury uptake and trophic transfer by marine plankton. *Environmental Science & Technology.* https://doi.org/10.1021/acs.est.7b03821.

Trophic Transfer of Monomethylated Mercury

Studies measuring naturally occurring stable isotopes of carbon and nitrogen, used to indicate trophic position in the food web, in parallel with MMeHg concentrations, have shown that MMeHg in marine fish rise with trophic level (Blum et al., 2013). However, other factors influence concentrations of MMeHg in marine fish, including physical factors such as proximity to coastline, depth of the feeding, geographic location, as well as those associated with fish biology, that is, sex, reproduction, life stage, ingestion rates and growth (AMAP/UNEP, 2018; Eagle-Smith et al., 2018; Lee and Fisher, 2016; Schartup et al., 2017). There has been relatively few investigations on these effects. For example, taxonomically similar fish that feed on mesopelagic fish, that is, in deeper parts of the ocean have been shown to carry higher burdens of MMeHg compared to their surface-feeding counterparts (Blum et al., 2013; Choy et al., 2009). This observation has been confirmed by the signatures of naturally occurring Hg stable isotopes accumulated in the tissues of the predatory fish as well as their prey. Higher concentrations of Hg have been found in fish of northern populations in comparison to their southern counterparts (Baumann et al., 2017), while computation of Hg bioconcentration factors, relating the concentrations in fish tissues to that of seawater have not shown any meaningful geographic patterns. Further research in the area of marine MMeHg bioaccumulation is much needed to provide sound advice to seafood consumers, health care managers as well as political leaders whose decisions impact the health of human populations around the world (AMAP/UNEP, 2018; Eagle-Smith et al., 2018; USEPA, 2018).

Human Exposure to Monomethylmercury

From the human perspective, marine fish consumption is of greatest concern as the majority of people are exposed to MMeHg via this route (Eagle-Smith et al., 2018). As mentioned above, MMeHg accumulates in organisms over time and is efficiently

transferred between trophic levels, reaching the highest concentrations in apex predators. Therefore, long-lived piscivorous fish contain the highest levels of Hg, almost entirely as MMeHg (Eagle-Smith et al., 2018; USEPA, 2018). Various advisories list tunas, sharks, swordfish and other top predatory fish as species to avoid eating as their flesh contains highest levels of MMeHg. However, fish is an important component of a human diet as it contains beneficial omega-3 fatty acids and essential nutrients and elements such as selenium. Selection of species for consumption should therefore be made based on expected MMeHg and other pollutant concentrations, relative to those of beneficial compounds, as well as species sustainability.

Recommended articles   Citing articles (0)

References

AMAP/UNEP, 2018   AMAP/UNEP
Technical background report for the global mercury assessment
http://www.mercuryconvention.org/Resources/Information/Publications/tabid/3429
US/Default.aspx (2018)
(in press)
Google Scholar

Amos et al., 2015   H.M. Amos, J.E. Sonke, D. Obrist, N. Robins, N. Hagan, H.M. Horowitz, R.P. Mason, M. Witt, I.M. Hedgecock, E.S. Corbitt, E.M. Sunderland
Observational and modeling constraints on global anthropogenic enrichment of mercury
Environmental Science & Technology, 49 (2015), pp. 4036-4047,
10.1021/es5058665
CrossRef   View Record in Scopus   Google Scholar

Baumann et al., 2017   Z. Baumann, R.P. Mason, D.O. Conover, P.H. Balcom, C.Y. Chen, K.L. Buckman, N.S. Fisher, H. Baumann
Mercury bioaccumulation increases with latitude in a coastal marine fish (Atlantic silverside *Menidia menidia*)
Canadian Journal of Fisheries and Aquatic Sciences, 74 (2017), pp. 1009-1015,
10.1139/cjfas-2016-0396
CrossRef   View Record in Scopus   Google Scholar

Blum et al., 2013   J. Blum, B.N. Popp, J.C. Drazen, C.A. Choy, M.W. Johnson

Methylmercury production below the mixed layer in the North Pacific Ocean
Nature Geoscience (2013), 10.1038/NGEO1918
Google Scholar

Bowman et al., 2015   K.L. Bowman, C.R. Hammerschmidt, C.H. Lamborg, G. Swarr
Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections
Deep-Sea Research Part II, 116 (2015), pp. 251-261
Article   Download PDF   View Record in Scopus   Google Scholar

Charlotte et al., 2018   R. Charlotte, *et al.*
Methylmercury speciation and dimethylmercury production in sulfidic solutions
Environmental Science: Processes & Impacts (2018), 10.1039/C7EM00533D
Google Scholar

Choy et al., 2009   C.A. Choy, B.N. Popp, J.J. Kaneko, J.C. Drazen
The influence of depth on mercury levels in pelagic fishes and their prey
Proceedings of the National Academy of Sciences of the United States of America, 106 (2009), pp. 13865-13869, 10.1073/pnas.0900711106
CrossRef   View Record in Scopus   Google Scholar

Driscoll et al., 2013   C.T. Driscoll, R.P. Mason, H.M. Chan, D.J. Jacob, N. Pirrone
Mercury as a global pollutant: Sources, pathways and effects
Environmental Science & Technology, 47 (2013), pp. 4967-4983
CrossRef   View Record in Scopus   Google Scholar

Eagle-Smith et al., 2018   C.A. Eagle-Smith, E.K. Sibergeld, N. Basu, P. Bustamante, F. Diaz-Barriga, W.A. Hopkins, K.A. Kidd, J.E. Nyland
Modulators of mercury risk to wildlife and humans in the context of rapid global change
Ambio, 47 (2018), pp. 170-197
Google Scholar

Gosnell et al., 2017   K.J. Gosnell, P.H. Balcom, C. Tobias, W.P. Gilhooly, R.P. Mason
Spatial and temporal trophic transfer dynamics of mercury and methylmercury into zooplankton and phytoplankton of Long Island sound
Limnology and Oceanography, 62 (2017), pp. 1122-1138
CrossRef   View Record in Scopus   Google Scholar

Hsu-Kim et al., 2018   H. Hsu-Kim, C.S. Eckley, D. Acha, X. Feng, C.C. Gilmour, S. Jonsson, C.P.J. Mitchell, *et al.*
Challenges and opportunities for managing aquatic mercury pollution in altered landscapes
Ambio, 47 (2018), pp. 141-169
CrossRef   View Record in Scopus   Google Scholar

Jonsson et al., 2014   S. Jonsson, U. Skyllberg, M.B. Nilsson, E. Lundberg, A. Andersson, E. Bjorn
Differentiated availability of geochemical mercury pools controls methylmercury levels in estuarine sediment and biota
Nature Communications, 5 (2014)
Art. # 4624
Google Scholar

Jonsson et al., 2016   S. Jonsson, N.M. Mazrui, R.P. Mason
Dimethylmercury formation mediated by inorganic and organic reduced sulfur surfaces
Scientific Reports, 6 (2016)
Art. # 27958
Google Scholar

Lee and Fisher, 2016   C.-S. Lee, N.S. Fisher
Methylmercury uptake by diverse marine phytoplankton
Limnology and Oceanography, 61 (2016), pp. 1626-1639, 10.1002/lno.10318
CrossRef   View Record in Scopus   Google Scholar

Lee and Fisher, 2017   C.-S. Lee, N.S. Fisher
Bioaccumulation of methylmercury in a marine copepod
Environmental Toxicology and Chemistry, 36 (2017), pp. 1287-1293
CrossRef   View Record in Scopus   Google Scholar

Mason, 2015   R.P. Mason
Geomicrobiology of mercury
H.L. Ehrlich, D. Newman, A. Kappler (Eds.), Ehrlich's Geomicrobiology (6th edn.), CRC Press, Boca Raton, FL (2015), pp. 323-342
(Chapter 16)
CrossRef   View Record in Scopus   Google Scholar

Obrist et al., 2018   D. Obrist, J.L. Kirk, L. Zhang, E.M. Sunderland, M. Jiskra, N.E. Selin

A review of global environmental mercury processes in response to human and natural perturbations: Changes of emissions, climate, and land use
Ambio, 47 (2018), pp. 116-140
CrossRef   View Record in Scopus   Google Scholar

Parks et al., 2013   J. Parks, A. Johs, M. Podar
The genetic basis for bacterial mercury methylation
Science, 339 (6125) (2013), pp. 1332-1335, 10.1126/science.1230667
CrossRef   View Record in Scopus   Google Scholar

Podar et al., 2014   M. Podar, C.C. Gilmour, C.C. Brandt, A. Soren, S.D. Brown, B.R. Crable, A.V. Palumbo, A.C. Somenahally, D.A. Elias
Global prevalence and distribution of genes and microorganisms involved in mercury methylation
Science Advances, 1 (2014)
Art # e1500675
Google Scholar

Schartup et al., 2017   A.T. Schartup, A. Qureshi, C. Dassuncao, C.P. Thackray, C. Harding, E.M. Sunderland
A model for methylmercury uptake and trophic transfer by marine plankton
Environmental Science & Technology (2017), 10.1021/acs.est.7b03821
Google Scholar

Stenzler et al., 2017   B. Stenzler, A. Hinz, R. Ruuskanen, A.J. Poulain
Ionic strength differentially affects the bioavailability of neutral and negatively charged inorganic Hg complexes
Environmental Science & Technology, 51 (2017), pp. 9653-9662,
10.1021/acs.est.7b01414
CrossRef   View Record in Scopus   Google Scholar

USEPA, 2018   USEPA (2018) Guidelines for eating fish that contain mercury.
https://www.epa.gov/mercury/guidelines-eating-fish-contain-mercury; (accessed 25.03.18).
Google Scholar

Further Reading

Hammerschmidt et al., 2013   C.R. Hammerschmidt, M.B. Finiguerra, R.L. Weller, W.F. Fitzgerald

Methylmercury accumulation in plankton on the continental margin of the Northwest Atlantic Ocean
Environmental Science & Technology, 47 (2013), pp. 3671-3677, 10.1021/es3048619
CrossRef   View Record in Scopus   Google Scholar

Glossary

Anoxic
An environment devoid of oxygen

Archea
A group of single-celled prokaryotic organisms that have distinct molecular characteristics separating them from bacteria, as well as from eukaryotes

Anthropogenic inputs
Human-related inputs to the environment

Bioaccumulation/bioconcentration
The accumulation of a compound (here mercury compounds) in the tissues of an organism. Efficient bioaccumulation may result in biomagnification of a compound in the food web. Biomagnification occurs when concentration of accumulated compound is higher in predator than in its prey

Demethylation
The decomposition of methylated mercury compounds into inorganic mercury

Dissolved organic carbon
The overall concentration of organic compounds, calculated based on the carbon content, of water after filtration

Gas evasion
The transfer of a gas from the water to the atmosphere under conditions of its supersaturation in the water

GEOTRACES
An international program quantifying the concentrations of trace elements and their isotopes in the ocean

Mer operon

A series of genes that code for the degradation of organic mercury compounds and the reduction of ionic mercury to elemental mercury

Metazoan

This group comprises all animals having the body composed of cells differentiated into tissues and organs and usually with a digestive cavity lined with specialized cells

Methylation

The conversion of inorganic mercury into methylated mercury compounds

Methylators

Microorganisms that methylate mercury

Minamata convention on mercury

A ratified United Nations Convention that is designed to reduce the inputs of mercury to the environment and to monitor these changes

Photochemistry

Reactions mediated by sunlight in water

Piscivorous

Fish eating organisms

Remineralization

The decomposition of particulate organic matter releasing nutrients and other elements back into the dissolved phase

Thermocline

The part of the ocean where the temperature changes dramatically from that of warm surface waters to that of cold deeper waters

Trophic level

The *trophic level* of an organism is the number of steps it is from the base of the food chain. Trophic transfer is the movement of a chemical from one trophic level to the next