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Mercury Biogeochemical Cycling: A Synthesis of Recent Scientific Advances

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Abstract

The focus of this paper is to briefly discuss major advances in scientific thinking regarding: 1-processes governing the fate and transport of mercury in the environment; 2- advances in measurement methods; and 3-how this fits in within the context of the Minamata Convention. Details regarding the information summarized here can be found in additional papers associated with this Virtual Special Issue of STOTEN.

Keywords Minamata Convention, mercury isotopes, methylmercury, fluxes, archives, wildlife

1. Introduction

Mercury (Hg) is a unique element, being one of two that exist as a liquid at ambient conditions, the other being bromine. Because of the presence of Hg as a liquid, it is volatilized to the atmosphere from terrestrial- and aquatic-based surfaces. Elemental Hg is considered to be fairly inert and is transported globally by way of the atmosphere. However, elemental Hg can be deposited to the surfaces fairly quickly once emitted (Miller and Gustin, 2013; Gustin et al., 2013). Elemental Hg is oxidized by a variety of compounds and Hg (II) compounds have a higher deposition velocity than elemental Hg (Ariya et al., 2015). Mercury is ubiquitous in the atmosphere and atmospheric concentrations have increased since the onset of civilization (Amos et al., 2013).

Given the volatility of elemental Hg and lack of long term sinks, once an atom of Hg is released to the atmosphere it can remain in circulation for > 1000 years (Figure 1). The only true sink is burial in ocean sediment and soil (Amos et al., 2013). Prior to development of human populations, major sources of Hg to the air included volcanic eruptions, emissions from rocks and soil enriched in Hg, and re-emission of that deposited to surfaces, coal burning events (Burger et al., 2019), and forest fires (Webster et al., 2016). Prior to humans, the major sink would have been uptake by plants. With the appearance of humans Hg would be mined and used for a variety of things.

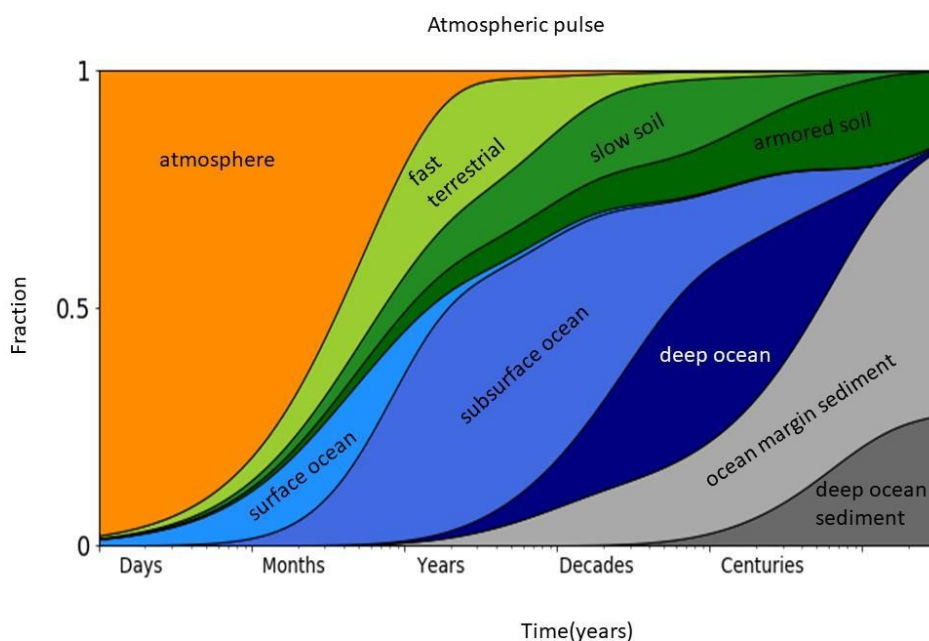


Figure 1. From Dr. Elsi Sunderland modified from Amos et al. 2013 The y-axis represents a unit pulse of Hg released to the atmosphere and the x-axis depicts how it partitions over time. Note that the figure represents a unit pulse of Hg as the perturbation, thus is independent of historical emissions estimates and meant to illustrate the timescales involved in Hg movement through environmental reservoirs.

Values in archives before 2000 BC, as proposed by Amos et al. (2013), are considered to reflect pre-anthropogenic emissions. After this time, civilizations utilizing Hg and biomass burning, potentially caused by humans, would have released Hg to the air. Mercury has been used by societies for at least 2500 years. It is found in Egyptian tombs & amalgams dating back to ca. 500 BC. Greeks & Romans used it for medicine

and cosmetics, and China's first emperor (Qin Shi Huang 221–210 BCE) was buried within a moat of Hg. Prior to the industrial revolution major sources were silver, gold, and cinnabar mining (Outridge, P. M. et al. 2018). Primary anthropogenic emissions of Hg to the atmosphere are currently considered to be artisanal gold mining>fossil fuel combustion> nonferrous metal and cement production (UNEP Global Mercury Assessment, 2013).

The biogeochemical cycle of an atom of Hg starts with the emission from natural and anthropogenic sources. Once emitted an atom of Hg enters the global atmospheric pool. This atom may be deposited to surfaces and then re-emitted. It also may be actively taken up by plants that sequester 1/3rd of the Hg emitted each year (Arnold et al., 2018). It also may be oxidized in the air promoting deposition. This Hg may be sequestered, converted to methyl- or di-methylmercury, or reduced and re-emitted back to the atmosphere.

Mercury pollution is an important environmental and public health issue. In August 2017, the United Nation's Minamata Convention on Mercury entered into force. The Minamata Convention on Mercury is legally binding and is the main international policy instrument for managing anthropogenic Hg emissions (air) and releases (water) to the environment, and to also protect human health (Minamataconvention.org). At the foundation of the successful implementation of the Minamata Convention on Mercury is the use of recent policy relevant science that have furthered our understanding of Hg biogeochemical cycling and its impacts on humans and terrestrial and marine ecosystems (Bank 2020). Here we synthesize recent scientific advances (discussed in detail in this issue) in understanding Hg biogeochemical cycling and outline critical topics and research avenues to guide future investigations and efforts.

2.0 Results and Discussion

2.1 Utility of stable mercury isotopes for understanding sources and processes

Due to the pioneering work of Professor Joel Blum and others in early 2000s, Hg stable isotopes have become an important tool used to understand sources of Hg contaminating any component of an ecosystem and processes affecting the fate and transport of Hg in the environment. Several review papers have recently been published on this topic (e.g., Bergquist and Blum, 2009; Yin et al., 2010; Blum et al, 2011; Kritee et al., 2013; Blum et al., 2014; Yin et al., 2014; Sun et al., 2016; Blum and Johnson, 2017; Buchachenko, 2018). See Tsui et al. 2019, this issue for basic systematics for Hg isotopes and discussion of fractionation processes as well as advancements in measurements.

The utility of stable Hg isotopes is greater than many other common isotope tracers such as stable carbon and nitrogen isotopes, because mass-dependent fractionation (MDF) and mass independent fractionation (MIF) can change the natural abundance of isotope ratios that can be used to understand complex biogeochemical processes of Hg occurring. MDF occurs during many biogeochemical processes such as abiotic and biotic redox reactions, changes in Hg chemistry, and phase changes (e.g., volatilization). MIF mainly occurs during photochemical transformations and Hg^(II) thiol complexation. Large-magnitude odd mass MIF (¹⁹⁹Hg, ²⁰¹Hg) occurs due to photochemical reactions (e.g., photoreduction and photodemethylation) mediated by the magnetic isotope effect while small-magnitude odd mass MIF may occur in the dark associated with the nuclear volume effect; even mass MIF (²⁰⁰Hg, ²⁰⁴Hg) originates from photochemical reactions potentially occurring in the upper atmosphere. The latter is not well understood, but is thought to be due to gas phase photochemical oxidation of elemental Hg (Berquist, 2018). With an understanding of processes causing fractionation and the signature of specific sources, Hg isotope mixing models can be used to determine the contribution of Hg from different sources occurring in soils, sediments, and surface water, etc. Since Hg isotopes often undergo both MDF and MIF in the environment, this provides a unique opportunity to use dual (i.e., MDF and odd-MIF) or even triple (i.e., MDF, odd-MIF, and even-MIF) isotope signatures that can be used to trace Hg in the environment.

More recently, an increasing number of studies measured Hg isotope ratios in animal consumers in food webs and inferred the isotope ratios to represent those of MeHg. Besides answering questions for the sources and transformation of MeHg in the specific ecosystems, these studies showed that stable Hg isotopes can have the potential, yet largely unexplored, in addressing fundamental ecological questions such as how energy is moved across ecosystem interfaces, and as a means of tracking animal movements (see Tsui et al., 2019). Tsui et al., 2019) reviews the use of Hg isotopes in ecology and biogeochemistry. This thorough paper provides much useful information and provides suggestions for future work to use Hg isotopes to tackle research questions unrelated to Hg.

As described throughout this special issue, Hg isotopes are useful in understanding many biogeochemical processes and have expanded our understanding of Hg cycling in the environment, which provides novel information to supplement the concentration and speciation analyses of Hg

currently utilized in the majority of Hg research studies. A current limitation is the concentrations needed to do isotope analyses are in the 5 to 10 ng range.

2.2 Importance of understanding fluxes

Measurement of concentrations are useful; however, concentrations alone do not allow you to understand processes for this flux needs to be measured. Flux is the rate of movement of a material to or from a surface or through a specific area. Measurements of fluxes from surfaces to the atmosphere and vice versa are done using flux chambers and micrometeorological methods. This has been done primarily for gaseous elemental Hg. For details see Sommar et al. this issue.

Novel dynamic flux chamber (DFCs) designs (Lin et al., 2012) have produced a uniform surface friction velocity that enables rescaling of the measured gaseous elemental Hg flux taking the effect of atmospheric turbulence into account. Results from novel DFC measurement campaigns were comparable with independent non-intrusive micro-meteorological (MM) flux methods (Zhu et al., 2015; Osterwalder et al., 2018).

A single-detector relaxed eddy accumulation system for synchronous measurement of gaseous elemental flux at one height has been constructed to mitigate for potentially large uncertainties deriving from intermittent sampling or sequential concentration measurements at different heights (Osterwalder et al., 2016). Recent work using this method has yielded unexpected results, such as emission as being the current dominant flux from peat bogs (Osterwalder et al.). Hg⁰ dry deposition is now recognized as the major component of the total Hg deposition in remote areas. Dry deposition of Hg⁰ via plant uptake displays profound dominance in terrestrial vegetated ecosystems with divalent Hg in gaseous or particulate phase making a minor contribution (Jiskra et al., 2018; Obrist et al., 2017; Wang et al., 2016).

There are developmental advances in implementing eddy covariance, the preferred and only direct MM method, to determine terrestrial Hg⁰ fluxes over background (Osterwalder et al., 2019) and contaminated sites (Pierce et al., 2015). Relatively low-cost Hg passive air samplers (MerPAS) have been deployed to capture vertical Hg⁰ concentration gradients in various landscapes to qualitatively address their role as Hg⁰ sources or sinks (Jeon and Cizdziel, 2019).

A new method has been developed for measurement of gaseous oxidized Hg flux using field chambers (Miller et al., 2018). In addition, measurement of dry deposition of oxidized Hg can be done using passive samplers providing information on deposition velocities that provides a pathway for better understanding chemistry of GOM compounds (Huang et al., 2015b and 2017). Recent improvement in quantification and compound identification of reactive mercury (RM) in the atmosphere using the University of Nevada, Reno-Reactive Mercury Active System (UNR-RMAS 2.0) will help to better constrain RM deposition rates (Gustin et al., 2019; Luippold et al., 2020).

Improved process-based understanding of the GASEOUS ELEMENTAL HG flux has been achieved by using stable Hg isotope fingerprinting (Enrico et al., 2016; Jiskra et al., 2019b; Jiskra et al., 2015; Obrist et al., 2017; Yuan et al., 2019). Day-resolved sampling of GASEOUS ELEMENTAL HG isotopic ratio in ambient air is now feasible (Fu et al., 2014; Jiskra et al., 2019a). Hg stable isotope ratios of samples involved in atmosphere-terrestrial interaction provide in combination with concentration and/or flux measurements novel constraints to quantitatively and qualitatively assess the bi-directional gaseous elemental flux (Obrist et al., 2017; Yuan et al., 2019).

Top-down approaches using inverse modeling have more widely been implemented to estimate fluxes (emissions) involving the balancing of sources and sinks while reproducing long-term atmospheric concentration records (Denzler et al., 2017; Denzler et al., 2019; Song et al., 2015). Initial steps were taken to validate gaseous elemental flux parameterizations commonly used in major chemical transport models (CTM) with long-term ecosystem level micrometeorological GASEOUS ELEMENTAL HG flux measurements (Khan et al., 2019).

2.3 Understanding methylation

Microbial mercury methylation is particularly susceptible to the changing environment, as the two key factors controlling methylmercury (MeHg) production from this natural process, i.e. microbial activity and Hg bioavailability, are both strongly affected by the environmental parameters (Hsu-Kim et al., 2018; Hsu-Kim et al., 2013). As such, previously unexpected 'hotspots' of MeHg accumulation may emerge when the aquatic environments are subject to climate changes and anthropogenic alterations. In recent years, research progress has been made in experimental and analytical techniques to accommodate the needs of identifying and quantifying the potential occurrence of microbial MeHg production in aquatic settings. These collective research efforts have greatly advanced our mechanistic

understanding in the heterogeneous distribution of MeHg as well as the disproportion between MeHg and total Hg under diverse and dynamic environmental conditions (Hong et al, this issue).

The discovery of the *hgcAB* genes provides the genetic basis for assessing Hg methylation from molecular biological perspectives (Parks et al., 2013). With the applications of clone libraries, Illumina sequencing of 16S rRNA amplicon and shotgun metagenomic analysis, the *hgcAB* gene clusters have thus far been proven effective biomarkers in examining complex matrices for the abundance of a diverse variety of Hg methylating communities (Bae et al., 2014; Bae et al., 2019; Bouchet et al., 2018; Gilmour et al., 2013; Jones et al., 2019; Podar et al., 2015). The microbial groups that possess the *hgcAB* genes are regarded as potential Hg methylators, predominantly sulfate reducing bacteria, iron reducing bacteria, methanogens and syntrophs, which are widespread in both natural and engineered aquatic systems (Gilmour et al., 2013; Liu et al., 2018; Parks et al., 2013; Podar et al., 2015). Despite the substantially different physical and chemical conditions among these microbial habitats, including extreme environments, none of the methylating taxa appear to be uniquely tied to any specific ecological niche. Given the prevalent co-occurrence of these microbial taxa in aquatic environment, it is important to understand how the interplay among these Hg methylating microorganisms influence MeHg production, and this knowledge should be widely applicable.

Methods for quantitatively assessing the bioavailability of inorganic Hg for microbial methylation have recently evolved from chemical equilibrium modeling (Benoit et al., 1999) and selective extractions (Ticknor et al., 2015) to approaches using enriched stable isotope tracers (Jonsson et al., 2014), whole-cell biosensors (Chiasson-Gould et al., 2014) and diffusive gradient thin films (DGT) (Ndu et al., 2018). The simultaneous application of multiple stable Hg isotopes allows proper simulation of environmental matrices containing an array of geochemically relevant inorganic Hg species, such as dissolved complexes, nanoparticles and bulk minerals (Jiskra et al., 2014; Jonsson et al., 2014; Jonsson et al., 2012; Liem-Nguyen et al., 2016). These isotopically labeled Hg species have been utilized in experimental studies, ranging from bench-scale incubations to mesocosm and ecosystem investigations (Bridou et al., 2011; Hintelmann et al., 2002; Jonsson et al., 2014; Rodríguez Martín-Doimeadios et al., 2004). DGT can also be utilized in such matrices to evaluate the relative chemical lability of different Hg species (Merritt and Amirbahman, 2007; Ndu et al., 2018), particularly after the designs of the diffusion phase and binding phase of DGT are optimized to enhance Hg binding capacity and selectivity. Enriched Hg isotopes may be coupled with whole-cell biosensors to assess the cellular uptake and subcellular distribution of

various Hg species during methylation (Butler et al., 2017). The application of whole-cell biosensors in Hg methylation research is currently limited by the lack of mechanistic information regarding the specific pathways of Hg uptake prior to methylation. Yet, recent finding that divalent metal transporters of methylating bacteria may be involved in Hg uptake (Lu et al., 2018; Schaefer et al., 2014) has shined the light on better construction of biosensors that well mimic microbial Hg methylation processes. Overall, these new techniques along with others have come to aid the ongoing research on mercury bioavailability, which has begun to recognize the essential roles of kinetically labile Hg species and interfacial reactions in dictating the methylation potential of ubiquitous inorganic Hg (Jiskra et al., 2014; Ndu et al., 2018; Stenzler et al., 2017).

2.4 Recent advances in understanding atmosphere chemistry and the implications with respect to input to ecosystems

Preconcentration on gold traps, followed by desorption into an atomic fluorescence detector, remains by far the most common method to measure elemental Hg, though other methods are sometimes used (cf. Albuquerque et al., 2017; El-Feky et al., 2018; Hynes et al., 2017; Kalinchuk et al., 2018; Lian et al., 2018). As the bias in KCl denuder-based measurements of oxidized Hg has become well-known (Bu et al., 2018; Cheng and Zhang, 2016; Gustin et al., 2015; Lyman et al., 2016), several alternative methods have emerged (Bu et al., 2018; Gratz et al., 2015; Huang and Gustin, 2015a; Miller et al., 2019; Slemr et al., 2018; Urba et al., 2017). Of these, cation-exchange membrane methods are the most widely used. Cation-exchange membrane methods include (1) direct laboratory analysis of the amount of oxidized Hg collected on membranes (Huang and Gustin, 2015a; Huang et al., 2013; Miller et al., 2019) and (2) dual-channel systems that determine the oxidized Hg concentration as the difference between an air stream that passed elemental Hg through membrane and one passed air through a pyrolyzer to determine total Hg (Ambrose et al., 2013; Gratz et al., 2015; Gustin et al., 2019; Lyman and Jaffe, 2012). Methods to identify oxidized Hg species are under development. An indirect method that determines speciation based on thermal desorption profiles from nylon membranes has yielded interesting and defensible results (Huang and Gustin, 2015a; Luippold et al., 2020), and mass spectrometry-based methods are being explored (Jones et al., 2016; Khalizov et al., 2018).

Our understanding of the behavior of Hg in the atmosphere has advanced in several ways over the past few years. A growing body of computational research has determined likely mechanisms by which elemental Hg is oxidized and oxidized Hg is reduced (Dibble et al., 2012; Dibble and Schwid, 2016; Jiao and Dibble, 2017a, b; Lam et al., 2019; Saiz-Lopez et al., 2019; Saiz-Lopez et al., 2018; Sitkiewicz et al., 2016; Sitkiewicz et al., 2019), and this research is narrowing down the field of probable Hg compounds in the atmosphere. Current computational work predicts that atmospheric oxidized Hg will be dominated by HgBrOH and HgBr₂ (Saiz-Lopez et al., 2019). Indirect thermal desorption methods point to a more diverse array of atmospheric Hg compounds. Work using nylon membranes has demonstrated that there are multiple compounds in the atmosphere and these vary across space and time, and are dependent upon the oxidants present in the atmosphere (Luippold et al. submitted, Huang and Gustin, 2015b; Huang et al., 2017). This is important information, because each compound has unique chemistry that will influence, how it can be measured, and the deposition velocity and availability to ecosystems, as well as potential for methylation.

Recent experimental evidence showed that MeHg forms from inorganic Hg via abiotic processes within cloud and fog droplets (Li et al., 2018). Another area with recent advances, especially in China, is understanding of the properties of Hg bound to particulate matter. During extreme particle pollution events in Chinese cities, the ratio of Hg mass to total particle mass appears to increase (Chen et al., 2016), compounding health risks. Also, studies around the world have shown a bimodal distribution of particulate mercury, with a significant fraction occurring in the coarse mode (Chen et al., 2016; Fang et al., 2010; Feddersen et al., 2012; Wang et al., 2019).

Many studies show that ambient atmospheric Hg concentrations are declining (Martin et al., 2017; Marumoto et al., 2019; Navrátil et al., 2018; Zhang et al., 2016), though this appears not to be the case universally (Fu et al., 2015; Martin et al., 2017). Declining Hg will, in general, mean declining ecosystem impacts, but the timing and spatial aspects of those changes are uncertain because atmospheric impacts to the surface are complex. Several recent whole-ecosystem studies have investigated Hg concentrations in various environmental compartments and transfer rates of Hg between compartments (Du et al., 2018; Zhou et al., 2018), including stable isotope studies (Enrico et al., 2016; Zhu et al., 2016) that have elucidated the ultimate atmospheric sources of Hg in those compartments. These kinds of studies are improving understanding of the mechanisms by which Hg in the atmosphere ultimately leads to health effects for humans and other organisms.

2.5 The marine biogeochemical cycle of Hg in light of recent advances in knowledge

In this special issue, Bowman et al. highlight insights on Hg cycling gained from analysis of seawater sampled during cruises over the last three decades, especially those that cut large swaths across major ocean basins and biogeochemical features. These efforts have greatly increased the number of measurements of Hg speciation in the ocean, and therefore, the information we have to explore and understand marine Hg biogeochemistry. The programs supporting some of these cruises, such as CLIVAR and GEOTRACES, also hosted scientists measuring many fundamental (temperature, salinity, oxygen, nutrients, pH, dissolved CO₂) and more specialized (trace elements and isotopes) parameters, providing a rich and unprecedented palette within which Hg results can be more deeply interpreted than 20 to 30 years ago. The synthesis- and interpretation-phases of these recent interdisciplinary projects continue, and a few additional cruises are being proposed for coming years, but it is clear that some of the research community assumptions about how Hg is transformed in the ocean, and possibly other environs, may need to be re-examined. Our new understanding of Hg in the ocean required, and has resulted from, many analytical innovations to enable accurate and high-resolution sampling across all depths of the ocean. This included taking analytical equipment to sea and integrating continuous analyzers with underway water samplers and equilibrators (e.g., Andersson et al., 2008a; Andersson et al., 2008b; Andersson et al., 2011; Kuss et al., 2011; Mason et al., 2017; Soerensen et al., 2014). The analysis of methylated Hg species in seawater also was developed and streamlined for shipboard and high-throughput analysis (e.g., Baya et al., 2013; Bowman and Hammerschmidt, 2011; Cossa et al., 2011; Hammerschmidt and Bowman, 2012; Munson et al., 2014; Stoichev et al., 2002; Živković et al., 2017).

The highlights that Bowman et al. draw attention to include:

Mercury species exhibit nutrient-like distributions. Previous vertical profile measurements of Hg species hinted at nutrient-like distributions (low at the surface, increasing with depth; e.g., Fitzgerald et al., 2007), and most recent cruises have confirmed this vertical segregation in detail (e.g., Bowman et al., 2015; Bowman et al., 2016; Coale et al., 2018; Cossa et al., 2018a; Cossa et al., 2018b; Munson et al., 2015; Sunderland et al., 2009). Indeed, total, elemental and dimethyl Hg concentrations are often distributed like nutrients. In the case of total Hg, this appears to be due to biological uptake and removal from surface water by sinking particles that contribute Hg to deeper waters upon remineralization. For elemental and dimethyl Hg, however, low concentrations in surface water are more likely due to in-situ loss processes, either evasion or destruction, and higher concentrations at depth imply that they are actively created under those conditions. This last point is an area of active research.

Arctic Ocean distributions of mercury species are unique. Mercury cycling in the Arctic is of concern and scrutiny, because Arctic marine organisms often contain anomalously high Hg concentrations compared to analogous animal species at temperate latitudes (e.g., AMAP, 2011). In recent years, the US, Canada, and Germany have sponsored GEOTRACES cruises that occupied oceanographic stations in different areas of the Arctic Ocean (Agather et al., 2019; Heimbürger et al., 2015; Petrova et al., in press; Tesán Onrubia et al., 2020; Wang et al., 2018), and Hg measurements from each cruise showed that Hg concentrations are higher in surface relative to deep water in the Arctic Ocean, in contrast to other ocean basins. Furthermore, similar surface-enriched profiles have been observed in the Southern Ocean (Cossa et al., 2011), and methylated Hg species were observed to have shallow maxima as well. These findings implicate an important role for sea ice and watershed runoff in Hg cycling, including ice preventing evasion and therefore retaining Hg in seawater (Fisher et al., 2012; Sonke et al., 2018) and bring elevated concentrations of the highly bioaccumulative methylated forms closer to or into the photic zone, promoting uptake by plankton. The sea-ice-land cycling of Hg in the Arctic is complex and almost certainly affected by climate change, and these dynamics will need further modeling to better understand now, and importantly test empirically, future implications for Hg cycling in the Arctic Ocean. This work is in the process of being assimilated into models, but highlights the difficulty of studying an ocean basin that is undergoing a high degree of temporal change and is therefore a moving target for modelers.

Maxima in methylated mercury can be found outside of oxygen minimum zones. Much of the early Hg biogeochemical research was performed in freshwater and sediment, and observations there suggested that low- to no-oxygen conditions were required to make methylated Hg species, namely mono- and di-MeHg. While relatively high concentrations of MeHg (picomolar) are found in the mid-water oxygen minimum zones that are common in the ocean, recent cruises have documented relatively high concentrations of MeHg in shallower waters too (e.g., in surface waters and at the depth of the subsurface chlorophyll maximum), particularly when viewed as a percentage of total Hg (e.g., Hammerschmidt and Bowman, 2012). This observation challenges the view that MeHg can only be formed through the activity of obligate anaerobic microbes like sulfate- and iron-reducers. This also supports and extends the observation by Sunderland and colleagues (2009) that microbial activity, rather than low-oxygen, is a key variable predicting steady-state MeHg concentrations in the ocean. However, interiors of some marine particulates may have low-oxygen microzones within otherwise oxic water where anaerobic processes can

operate (Capo et al., 2020; Ortiz et al., 2015). Thus, the controlling variables for Hg methylation in much of the oceanic water column still need to be resolved. It is especially interesting to note that these shallow maxima are often associated with water columns that possess significant oxygen minima in deeper waters and could imply coupling of MeHg dynamics between surface and mid-waters in some way that we do not yet understand.

Insights from the incorporation of genomic information in marine mercury studies. Since the recent discovery of a pair of genes (*hgcAB*) required for Hg methylation in anaerobic prokaryotes (Parks et al., 2013), the hunt has been on for these genes in seawater (e.g., Bowman et al., 2020; Gionfriddo et al., 2016; Lin et al., in review; Podar et al., 2015; Villar et al., 2020). The data thus far indicate that the *hgcAB* gene sequences originally identified from cultured, obligate anaerobes are not found in the oceanic water column. However, there are some genes in the ocean that are similar (homologous) in their amino acid sequences in ways that are thought to be related to the Hg methylating ability coded by *hgcAB*. In some cases, the homologous sequence segments found in marine metagenomes can be tied back to specific taxa and implicate microbes that do not fit the previous view of the ecology of Hg methylators (Gionfriddo et al., 2016; Lin et al., in review; Villar et al., 2020). These efforts are just beginning and are not trivial (Christensen et al., 2019) and should be coupled to methylation assays (Munson et al., 2018; Wang et al., 2020) and done in collaboration with biogeochemical modeling (Archer and Blum, 2018; Semeniuk and Dastoor, 2017; Zhang et al., 2020). The synergistic combination of these efforts offers great potential for insight and an aid to experimental design and empirical evaluation.

2.6 Recent advances in understanding terrestrial Hg cycling

Methodological advances have been key in advancing the understanding of terrestrial Hg cycling. The advent of natural abundance isotope measurements has enabled the identification of Hg sources, how the inputs from different sources are transformed in the terrestrial environment (Yuan et al., 2019), and then how Hg is exported to food webs in surface waters as well as on land (Demers et al., 2018; Du et al., 2018). Microbial techniques have further contributed to the ability to resolve the biological dimension of the biogeochemical interactions that affect Hg cycling (Strickman et al., 2016, Liu et al., 2018). The other area of major advance is in micrometeorological techniques that document how changes in the terrestrial environment influence the bidirectional exchange of Hg between the atmosphere and terrestrial surfaces (Osterwalder et al., 2017, Sommar et al., 2020).

The most striking advance in the understanding of terrestrial Hg cycling is documentation of how climate warming is mobilizing the stores of Hg in Arctic and boreal soils due to both the thawing of permafrost (Schuster et al., 2018) and the increasing occurrence of wildfire (Kumar et al., 2018). This has raised the question as to whether these changes in the terrestrial environment might reverse the overall direction of global transport that previously moved Hg from warmer mid-latitudes to colder high-latitudes (Jiskra et al., 2018). The role of vegetation changes is thus increasingly recognized as a key terrestrial factor in global Hg cycling. Those vegetation changes can be both intentional due to management choices such as forestry, or unintended due to climate influences (greening or browning). Two human land use choices also are now recognized as affecting the exposure of wildlife as well as humans. One is through the cultivation of rice which bioaccumulates MeHg more effectively than other crops in contaminated landscapes (Abeyasinghe et al., 2017). The other land use factor is artisanal gold mining which releases much more Hg than previously estimated (Obrist et al., 2018). Land use and climate will thus have a bearing on how effective Minamata-related reductions in the outputs of Hg will be in changing the exposure of people and wildlife to Hg (Bishop et al., 2020).

As societies around the world moves forward with implementing the Minamata convention, the effectiveness of the measures in promoting recovery will remain a major question. While it has generally been believed that it will take generations of reduced Hg in the atmosphere to translate into reduced Hg export from terrestrial to aquatic ecosystems, there have been some intriguing indications that this aspect of recovery may occur on decadal scales (Gerson and Driscoll, 2016). This points to the value of continued and intensified monitoring of the fluxes of Hg within and between ecosystems using the improved methodological capabilities at our disposal. These include new micrometeorological techniques to resolve land-atmosphere exchange, as well as continuation and expansion of time-series measurements in soils, waters and the biota.

2.7 Mercury cycling in Freshwater systems

In their review of Hg cycling in freshwater systems, Branfireun and co-authors (this issue) frame their examination of our current state of knowledge about the cycling of Hg in lakes in the context of a widely accepted, but what they consider outdated, conceptual model. Although anoxic bottom waters and profundal sediments of stratified lakes have long been seen as the exclusive zone of methylation in freshwaters, they contend that this is more the exception than the rule. They suggest that littoral zones,

periphyton, biofilms, and the catchment as sources of MeHg to aquatic systems have not received the attention that they deserve, and may be critical to understanding the supply of MeHg to aquatic food webs now, and particularly in future climates. They also review the critical role of dissolved organic matter in freshwater systems in regulating aspects of MeHg supply at a range of scales, from the catchment to the cell wall. Their revised conceptual model of Hg cycling highlights these observations, and draws attention to what they consider to be the important scientific frontiers in research on the freshwater Hg biogeochemistry in the coming years.

2.8 Utility of archives for understanding past concentrations

Mercury research using natural archives, lake sediments and peat in particular, has become a well-established field, with consistent methodological (sampling and analytical) approaches. This research has contributed to the knowledge we have today on Hg cycling. Recently, additional advances have opened new possibilities and perspectives on past Hg cycling, by incorporating both new methodological applications and new types of archives. The most remarkable recent advancement is the inclusion of Hg isotopes. This technique has been applied to lake sediments, peat, marine sediments, ice cores, and tree rings. Mercury isotopic fractionation has revealed that lake sediments contain a mix of precipitation-derived and vegetation-bound Hg exported from the lake catchment (Cooke et al., 2013; Kurz et al., 2019; Chen et al., 2016). They have also allowed for discerning the dominant atmospheric (wet or dry) deposition mechanism in peatlands, and record global-scale changes in the chemistry of the atmosphere. A global-scale shift in the mass independent fractionation of odd Hg isotopes has been noted in some studies (odd-MIF) (Cooke et al., 2013; Yin et al., 2016) that has been interpreted as a change in the photochemistry of the atmosphere (Kurz et al., 2019).

As for the natural archives, the beginning of the 21st century has witnessed the initiation and surge of studies on Hg in tree rings (see references in Cooke et al., 2020; this special issue). Tree rings offer a time resolution that is hardly found in other archives, except for varved lake sediments, offering a new opportunity to study the past response of atmospheric Hg deposition to short-term changes in emissions. These studies demonstrate that uptake from air by foliage and translocation within the tree is the main pathway for Hg incorporation and, thus, tree ring Hg contents record gaseous elemental Hg concentrations in air. A second new archive worthy of mention is human bones (Rasmussen et al., 2008, 2015; Emslie et al., 2019; Walser et al., 2019), because this archive relates specifically to human health.

Recent research has shown that human bones from individuals living in rural areas, far from mining and metallurgy centres, recorded preindustrial changes in atmospheric mercury pollution synchronous with other markers of atmospheric pollution (i.e., lead and lead isotopes) and with the chronology established from natural archives in the region (López-Costas et al., 2020).

Decades of research have helped to establish temporal trends in atmospheric Hg deposition at various time scales, but they have equally shown that all archives are affected by (integrate) a range of processes and reflect different aspects of the Hg cycle. Lake sediment records of mercury accumulation are controlled by atmospheric deposition, sediment focusing, fluxes from the catchment (runoff of eroded soil and subsurface discharge) and catchment size, morphology and land use; peat records are affected by atmospheric dust deposition, catchment fluxes (in minerogenic mires), biotic uptake, and internal long-term and short-term processes (including peat decomposition); ice cores record mercury scrubbed during precipitation; and tree rings record atmospheric mercury concentrations. The realization of the complexity of the mercury cycle, that no archive represents an absolute record of past mercury deposition, and that several processes influence mercury cycling to a different extent in each archive, has prompted a need for integrated studies using various archives and multiproxy data, so to obtain information of the main drivers and processes. In a few cases, the application of statistical modelling (PCA and PLS) on multiproxy data, enabled to determine the weight of the drivers affecting mercury content in lake sediments (Rydberg et al., 2015) and peat (Pérez-Rodríguez et al., 2015).

Despite this apparent constraint, natural archives provide a consistent picture of the variations in atmospheric mercury through time. They show that, in most cases, preindustrial pollution was restricted to areas downwind or downstream of cinnabar or precious metal mining centres. The earliest evidence, Copper age (3250 BCE), of mercury pollution was recorded in river sediments from SW Spain, as a result of runoff from the Iberian Pyrite Belt 60 km upstream (Leblanc et al., 2000). But the earliest evidence of atmospheric mercury pollution was found in lake sediments from the Peruvian Andes in South America. Cooke et al., 2009) found elevated mercury concentrations in sediments dating to c. 1400 BCE. Despite the intense mining and metallurgy activity occurred during the Roman period, as attested by lead research in natural archives, there is little evidence of atmospheric mercury pollution. One such evidence was provided by the recent study developed on human bones (López-Costas et al., 2020), which showed higher Hg content in individuals from the Roman period compared to those from Antiquity, even in a rural area far away from urban and mining centres and upwind from emission sources. In any case, legacy Hg from

historical mining seems to be the main Hg source to lakes and marine coastal areas prior to the industrial period (Elbaz-Polichet et al., 2011; Bindler et al., 2012; Corella et al., 2017).

For the industrial period, most records show a significant and steady increase in Hg since the early 1800's to peak between the 1970's-1980's. Flux ratios increased on average 3- to 5-fold compared to preindustrial values. Although lower ratios are estimated from tree rings studies and, in areas impacted by point emissions sources, Hg loads remain elevated. Regional differences in Hg accumulation are also illustrated by research in Arctic lakes, frequently showing unexpectedly high Hg fluxes (Cooke et al., 2012; Drevnink et al., 2012; Muir et al., 2009).

Future research oriented to combine multiproxy data with systematic application of statistical modeling (generalized linear models, GLM, generalized additive models GAM, or structural equation models, SEM) may help to deal with the many factors and complex interactions between the drivers involved in regional Hg cycling. In the same way, extensive application of Hg isotopes to natural archives may also contribute to shed light into the nature of preindustrial and industrial era Hg emissions to the atmosphere.

2.9 Impacts on humans and wildlife

The paper by Chételat et al. (2020) presents a synthesis of theory and applied information for measuring and interpreting wildlife exposure to MeHg. Methylmercury concentrations in wildlife are the net result of ecological processes influencing dietary exposure combined with physiological processes in the body that regulate MeHg assimilation, transformation, and elimination. The review summarizes advances in both ecological and physiological research and their implications for interpreting wildlife MeHg concentrations. Ecological tracers can reveal often complex pathways of Hg exposure for wildlife that result from animal movement and migration, ontogenetic diet shifts, and cross-ecosystem feeding. Recent advances in the application of ecological tracers, such as fatty acids and compound-specific stable isotope analysis, are presented in the context of characterizing dietary MeHg exposure. Physiological research shows vertebrate species and tissues can differ markedly in their capacity to eliminate MeHg. Biological factors such as age, sex, life history, maternal transfer, and changes in body mass are also highly relevant. Important distinctions for the selection of tissues for sampling are discussed including whether they are inert or physiological active, act as sites of storage, transformation or excretion, as well as the period of MeHg exposure they represent. Non-lethal external tissues such hair, toe nails, scales, and egg shells show promise as indicators of internal MeHg

concentrations, although caveats and recommendations for further validation are identified. Wildlife are useful indicators of biological exposure to MeHg, and the advances synthesized in this paper provide guidance for effectively assessing future efforts to reduce Hg releases and MeHg bioaccumulation in the environment.

2.10 Major advances in methods and knowledge for the assessment and remediation of contaminated sites.

Much of the research on Hg pollution has focused on its role as a global pollutant. Specifically, its wide distribution and deposition from the atmosphere, and subsequent landscape/ecosystem-scale processes impacting watershed mobilization, methylation, and bioaccumulation. Mercury can also be a local pollutant, where contemporary or historical industrial activities have resulted in directly released Hg to the land or water. These areas typically have Hg concentrations several orders of magnitude higher than background areas and the Hg speciation/forms present at these sites are often different from what occurs in areas primarily impacted by atmospheric deposition. Common examples of industrial-scale Hg contaminated sites include abandoned mines (mercury, gold, or silver) and chemical production facilities.

Recent advances in the assessment and remediation of industrially Hg contaminated sites provide opportunities to reduce the impacts of Hg pollution at a local scale (Eckley et al., 2020). For example, improvements in the detection of Hg using portable X-ray Fluorescence Spectrometers (XRF) allow for near real-time measurements of soil Hg concentration in this field. The use of XRFs can greatly increase the number of samples collected, which improves our understanding of the spatial extent and heterogeneity of contamination (McComb et al., 2014; Miller et al., 2013). Another recent advancement in contaminated site assessments is the use of Hg stable isotope fractionation to identify the contribution from specific industrial sources and help differentiate it from Hg deposited from the atmospheric pool (Donovan et al., 2013; Foucher et al., 2013; Yin et al., 2013). Source-attribution is possible because Hg can be imprinted with distinct isotopic signatures from different industrial processes and can be detected using a multi-collector ICP-MS.

In addition to identifying sources of Hg pollution, it is also important to understand the speciation of the Hg present. The use of X-ray absorption fine structure (XAFS) spectroscopy (which has recently improved detection limits for Hg) has been used to understand how Hg forms/speciation at Hg

contaminated sites can change in response to soil properties and redox conditions in ways that impacts its mobility and bioavailability for methylation (Manceau et al., 2015; Poulin et al., 2016). There have also been other recent methodological advances specifically aimed at understanding the sub-fraction of Hg that is more available for methylation. An example is the use of diffuse gradient in thin-film samples (DGT) that are designed to identify bioavailable fractions of Hg (Ndu et al., 2018). These methods are particularly important at Hg contaminated sites where the total-Hg concentrations may be very large, but the vast majority may be present in recalcitrant forms that have low bioavailability (Eckley et al., 2017; Kim et al., 2000).

In addition to methodological advances, there has also been an increased understanding of the important role that meteorological and hydrological conditions play in determining the mobilization of Hg from contaminated sites into the surrounding landscape via fluxes to the water and to the air. For water fluxes, it has become well established that episodic/seasonal periods of elevated discharge are the primary driver of Hg transport at many sites and that this transport is highly correlated with suspended sediment transport (Eckley et al., 2020). The importance of surface-air fluxes from contaminated sites has also become more apparent due to recent studies focused on developing models to scale fluxes spatially and temporally (Eckley et al., 2011; Kocman and Horvat, 2011; Miller and Gustin, 2013).

Traditional remediation approaches at Hg contaminated sites have focused on lowering total Hg concentrations through removal/dredging or capping with low Hg content materials. These efforts are most feasible for relatively small and highly contaminated areas. Alternative approaches have recently been developed that do not focus on decreasing total Hg concentrations, but instead focus on reducing MeHg production. These approaches can be more cost-effective than dredging/capping and are applicable over broader landscape areas. An important recent advancement has been the use of *in situ* amendments such as biochar, activated carbon (AC), thiol/sulfur modified materials, and iron. These amendments have been shown to reduce inorganic Hg availability for methylation by increasing sorption to the solid phase of sediment and reducing levels in pore water by up to 95% (Gilmour et al., 2018; Schwartz et al., 2019; Ting et al., 2018). However, site-specific sediment characteristics, such as the amount and quality of competing sorbents like dissolved organic matter, can have a large impact of the amendment effectiveness (Johs et al., 2019).

In addition to soil amendments, there are other remediation options that are aimed at reducing MeHg production. These can include the addition of oxygen or nitrogen to lake water to poise the redox conditions at levels above where methylation occurs (Matthews et al., 2013; McCord et al., 2016). In other scenarios, decreases in sulfate loading, carbon loading, or reservoir water-level management can be utilized to decrease MeHg production (Eckley et al., 2017; Hsu-Kim et al., 2018; Wasik et al., 2012). Overall, while contaminated site assessment and remediation remains complex, recent methodological advances and novel remediation strategies have used this complexity to identify opportunities to decrease the mobility and bioavailability of Hg (Eckley et al., 2020).

3.0 Conclusion Importance of understanding the above for achieving the goals of the Minamata Convention.

Recent scientific advances in Hg stable isotope chemistry and applications (Tsui et al., 2020) have important implications for the Minamata Convention especially in the context of source apportionment modeling studies near Hg hotspots (Kwon et al., 2020) and to identify ecosystems sensitive to and atmospheric deposition, Hg methylation, and efficient trophic transfer (Bank, this issue). These high-resolution analyses will also be critical for identifying natural and anthropogenic sources and the importance of different geochemical pools of Hg and MeHg in water, sediment, fish and subsequent MeHg exposure to humans (Bank, 2020). Temporal analyses of Hg stable isotopes can also be achieved by using archived samples (Lepak et al., 2019) to identify changes in Hg sources across spatiotemporal gradients. Furthermore, these approaches can be used within a global monitoring framework in support of the Minamata Convention effectiveness evaluation (Bank, 2020; Kwon et al., 2020).

Ecosystem sensitivity, as it relates to atmospheric deposition and subsequent methylation-demethylation dynamics and food web complexity, is an important theme that has been identified by the Conference of Parties with regard to the Minamata Convention effectiveness evaluation. Evaluating post depositional processes (Wang et al., 2010) and sources simultaneously, in a more integrated manner, will be required since atmospheric loadings of Hg do not always translate into higher MeHg concentrations in local, terrestrial biotic communities (Bank et al., 2005; Shanley et al., 2019; Bank, 2020). Evaluating ecosystem change, post depositional processes and food web characterization will be essential for tracking changes of MeHg in biota over time (Braune et al., 2014; Braune et al., 2016; Wang et al., 2010; Wang et al., 2019) which is an important aspect of the Minamata Convention effectiveness

evaluation. Therefore, valid temporal assessments of mercury in biota need to evaluate concomitant changes in food webs (Bank 2020).

Since Hg modeling of Hg in different ecosystem compartments has a very high degree of uncertainty (Selin, 2014; Gustin et al., 2016), and because forecasting is currently either extremely limited or not possible, moving forward researchers will need to increase transparency and inform policy makers that these models have important limitations, rely on hypotheses and, at times, have completely unrealistic assumptions. Furthermore, the Minamata Convention on Hg will benefit from treating Hg pollution as a seafood safety and food security issue (Bank, 2020) as this will engage an entire new discipline of researchers and policymakers to address this important environmental and public health problem.

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