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Review

Mercury transformation processes in nature: Critical knowledge gaps and perspectives for moving forward

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ABSTRACT

The transformation of mercury (Hg) in the environment plays a vital role in the cycling of Hg and its risk to the ecosystem and human health. Of particular importance are Hg oxidation/reduction and methylation/demethylation processes driven or mediated by the dynamics of light, microorganisms, and organic carbon, among others. Advances in understanding those Hg transformation processes determine our capacity of projecting and mitigating Hg

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risk. Here, we provide a critical analysis of major knowledge gaps in our understanding of Hg transformation in nature, with perspectives on approaches moving forward. Our analysis focuses on Hg transformation processes in the environment, as well as emerging methodology in exploring these processes. Future avenues for improving the understanding of Hg transformation processes to protect ecosystem and human health are also explored.

Introduction

Global concerns about mercury (Hg) are largely attributed to its long-range atmospheric transport mainly in the form of gaseous elemental Hg (Hg^0) (Schroeder and Munthe, 1998; Horowitz et al., 2017), biomagnification in the form of methylmercury (MeHg) in aquatic food webs (Amezcua et al., 2022; Lavoie et al., 2013; Tsz-Ki Tsui et al., 2019; Zhang et al., 2022), and toxicity especially neurotoxicity of MeHg. As a result, Hg can be accumulated in fish and marine mammals by a factor of up to ten millions when compared to its concentration in water, posing risks to ecosystem and human health even in the most remote regions (AMAP/UNEP, 2018). Among all processes governing Hg biogeochemistry and health risk, Hg transformation among its various chemical species plays a vital role. Hg exists in the environment and organisms in three oxidation states (i.e., Hg^0, Hg^I, Hg^{II}) and forms complexes with a large number of ligands including binding sites at the surfaces of particulate matter and cell membrane; different Hg species may have distinctive mobility, reactivity, bioavailability, and toxicity. Many of the transformation processes, especially those involving oxidation/reduction and methylation/demethylation are driven or mediated by the dynamics of light, microorganisms, and organic carbon. Those transformation processes determine Hg cycling in the environment and its entering into the biosphere. According to the Web of Science Core Collection (retrieved on July 8, 2022), publications on mercury involving topics of methylation (1,336), demethylation (321), oxidation (1,486), and reduction (2,062) accounted for 19% of all publications of Hg in the categories of environmental sciences (27,757).

Despite the advances made in the last few decades, key processes controlling mercury transformation in the environment and biosphere, especially those involving oxidation/reduction and methylation/demethylation, are far from clearly understood, which in turn hinders our ability to predict or mitigate mercury risks to ecosystem and human health. Here, we provide a critical analysis of major knowledge gaps in our understanding of Hg transformations in nature, with perspectives on approaches moving forward. Our analysis is organized around key questions related to both the methodology for studying Hg transformation processes and such processes in nature.

1. Mercury species and speciation in environmental systems

According to International Union of Pure and Applied Chemistry (IUPAC) recommendations in 2000, the chemical species of an element are described with respect to isotopic composition, oxidation state, inorganic/organic/macromolecular complexes, and organometallic structures (Templeton et al., 2000). This definition of “species” is based on chemical properties and is different from operational procedures (e.g., sequential extraction).

Mercury can occur in a variety of species in environmental and biological samples (Table 1). In recent years, increasing attention has been paid to the isotopic composition of Hg, which is a useful tool for tracking sources and transport and transformation processes (see Section 6). In general, total MeHg and total Hg (THg) are commonly analyzed, and then the concentration of inorganic Hg^{II} can be obtained by subtracting total MeHg from THg. The assumption here is that Hg in the sample is exclusively composed of inorganic Hg^{II} and MeHg.

As for the oxidation state of Hg, it can occur in three oxidation states: Hg^0, Hg^I, and Hg^{II}. From the perspective of a redox reaction, the oxidation of Hg^0 or the reduction of Hg^{II} should generally be a two-step single-electron transfer process. Usually, accepting or donating the first electron (i.e., $Hg^{II} + e^- \rightarrow Hg^I$ or $Hg^0 \rightarrow Hg^I + e^-$) is the rate-determining step for the whole redox reaction. However, due to the lone pair electron, Hg^I is metastable and is rarely identified and quantified in the redox transformation of Hg. In a simulation for gas-phase BrO-initiated oxidation of Hg^0, besides Hg^{II} species, Hg^I species (e.g., HgBr, HgBrO/HgOBr) were identified by mass spectrometry as important products in the condensed phase (aerosols and deposits) (Raofie and Ariya, 2004). Recent studies also identified Hg^I as an intermediate in poplar leave-mediated Hg^0 oxidation by using liquid chromatography-inductively coupled plasma–mass spectrometry (LC-ICP-MS), which occurs via a two-step single-electron transfer mechanism (Liu et al., 2021). It remains a challenge to develop mild extraction and separation for qualitative and quantitative Hg^I analysis in multi-matrices (Loria et al., 2022), including water, soil, sediment, and air, and reveal the occurrence of Hg^I and its importance in redox and methylation of Hg.

Among organomercurials, MeHg is undoubtedly the focal point; however, other organomercurials cannot be ignored. The occurrence, formation, and degradation of dimethylmercury (DMHg) are less well known. In addition, evidence has been provided in the past decades for the occurrence of other organomercurials, e.g., ethylmercury (EtHg) in the environment (Cai et al., 1997; Gao et al., 2008). The occurrence of EtHg has been reported in the Everglades (Cai et al., 1997; Mao et al., 2010), and other environments that are less affected by human activities (e.g., soil from Kejimkujik National Park in Canada (Siciliano et al., 2003) and Mt. Myoko in Japan (Kodamatani et al., 2018) and simulated redox soil environments (Beckers et al., 2019). These results suggest that EtHg

Table 1 – Mercury species in environmental and biological samples

Species of Hg	Example	Significance
Isotopic composition	Natural stable isotopes of Hg (average abundance): ^{196}Hg (0.15%), ^{198}Hg (9.97%), ^{199}Hg (16.87%), ^{200}Hg (23.10%), ^{201}Hg (13.18%), ^{202}Hg (29.86%), ^{204}Hg (6.87%)	Isotopic composition of Hg in samples is a powerful tool for tracking sources, transport, and transformation processes of Hg in the environment (Section 6)
Oxidation state	Hg^0, Hg^I, Hg^{II}	Hg^I, as an important redox intermediate, is metastable, and little is known for its occurrence and role in Hg transformation.
Inorganic/organic/macromolecular complexes	$Hg(OH)_2$, $HgCl_x^{(x-2)-}$, $Hg(Cys)_2$, Hg-phytochelatin, Hg-DOM, Hg-metallothionein	Due to the complexity of DOM composition and structure, the thermodynamics and kinetics of its complexation with Hg^{II}/MeHg need to be further clarified.
Organometallic complexes	Methylmercury (CH_3Hg^+), dimethylmercury (CH_3HgCH_3), ethylmercury ($CH_3CH_2Hg^+$), phenylmercury ($C_6H_5Hg^+$)	Little is known for organomercurials other than MeHg. Discussion on dimethylmercury please see Section 3. The occurrence, fate, bioaccumulation and toxicity of ethylmercury need to be further clarified.
Particulate Hg	Particle-bound Hg, HgS, HgSe	Particle-bound Hg(II) and MeHg are important factions of Hg in water column, although further clarification is needed for their bioavailability. Particle-bound Hg^0 is not purgeable, which affects the water-air exchange of Hg. The formation and dissolution of HgS and HgSe may play critical role in microbial intake, methylation, detoxification, and excretion. It is necessary to further develop methods to clarify the occurrence, transformation, and effects of particle-bound Hg^0, HgS, and HgSe. It is particularly important for characterization of size and crystal plane of HgS and HgSe.

Note: Cys, cysteine; DOM, dissolved organic matter.

may derive from natural sources in addition to anthropogenic activities (e.g., pesticide spray). With the use of derivatization other than ethylation (e.g., propylation and phenylation) in MeHg analysis, it is expected that the occurrence of EtHg in the environment will be more common than previously thought. Whether there are other yet-to-be-identified species of organomercurials in the environment needs to be further explored, on the basis of developing novel speciation methods.

As for particulate Hg, it is well known that Hg^{II} and MeHg can be bound with particulate matter in the water column, with their fractions dependent on the concentration and composition of particles. A recent study has shown that particle-bound Hg^0 account for 45%–80% of the total Hg^0 in Everglades water (Wang et al., 2015). As particle-bound Hg^0 is not purgeable, further studies are warranted to examine its role in the air-water exchange and global biogeochemical cycling of Hg. A simple and rapid qualitative and quantitative method for particle-bound Hg^0 needs to be further developed to elucidate its occurrence and environmental significance. In addition to particle-bound Hg, Hg can also occur in the solid phase. As one of the most thiophilic elements, Hg can exist as HgS and HgSe solids with different sizes and crystal planes and structures in environmental and biological samples (Chen et al., 2017; Dang et al., 2019). With the development of electron microscopy, single particle ICP-MS, and other (nano) particle characterization techniques, it is possible in practice to include HgS and HgSe in the chemical species of Hg and reveal their role in key processes such as microbial bioavailability, methylation, and demethylation (Cai et al., 2022; Khan and Wang, 2010; Liu et al., 2022; Luo et al., 2017; Tian et al., 2021).

To sum up, the connotation of chemical species of Hg includes isotopic composition, oxidation state, complexes, organometallic structures, as well as particulate species (e.g., HgS and HgSe). In the future, it is necessary to develop highly sensitive in-situ and ex-situ methods to characterize various Hg species. Particularly, the fourth-generation synchrotron radiation may play a key role in the highly sensitive in-situ characterization of Hg species. In ex-situ characterization, attention should be paid to:

1) **Optimization of extraction methods**. To better understand the speciation of Hg in the real environment, it is urgent to develop mild extraction methods that do not change the original species (which is particularly important for metastable Hg^I and particle-bound Hg^0) and have high selectivity and extraction efficiency (e.g., for the extraction of HgS and HgSe particles from solid matrices).
2) **Combination of novel technologies**. Particularly, it is necessary to develop online and offline analytical systems hyphenated with various detection methods, such as chromatography-element specific detection/molecular mass spectrometry/electron microscopy. We need to identify the full spectrum of Hg species in the environmental and biological samples, and therefore to have a full understanding of the biogeochemical cycle of Hg and the associated risks.

2. Atmospheric Hg transformations

The fate and residence time of atmospheric Hg are largely regulated by its inorganic speciation particularly Hg^0, Hg^I, and

Hg^{II}, which exhibit markedly different behaviors for gas-liquid and gas-particle partitioning, and deposition to the surface environment. The transformation between Hg^0 and Hg^{II} is through redox chemistry, i.e., oxidation and reduction, often initiated by sunlight and involves both heterogeneous and homogeneous reactions in the atmosphere. Redox chemistry is one of the most important chemical mechanisms applied in mechanistic models simulating global Hg deposition and distribution.

Over the past two decades, a consensus has been generally reached that oxidation of atmospheric Hg^0 occurs mainly as two-step, gas-phase reactions initiated by halogen atoms (mainly Br) and OH radicals, and involves Hg^I as an intermediate (Dibble et al., 2020; Holmes et al., 2010). The oxidation process is recognized with large spatial variation among different initiating oxidants: halogen-initiated oxidation dominates in the polar troposphere (Lindberg et al., 2001; Wang et al., 2019), marine boundary layer (Wang et al., 2014), boundary layer over salt lakes (Obrist et al., 2011) and subtropical free troposphere (Gratz et al., 2015), whereas OH-initiated oxidation plays an important role in the tropical free troposphere and continental boundary layer (Dibble et al., 2020; Gencarelli et al., 2017; Shah et al., 2021; Ye et al., 2016). Once Hg^I is formed, subsequent oxidation can occur with available secondary oxidants such as O_3, OH, Br, BrO, ClO, NO_2, and HO_2 (Calvert and Lindberg, 2005; Dibble et al., 2012; Goodsite et al., 2004; Jiao and Dibble, 2017; Saiz-Lopez et al., 2020; Wang et al., 2014). Still, uncertainties exist in spatially and temporally differentiating the contribution of various initiating oxidants (Br, OH, and other oxidants) from field campaigns, and in experimentally determining the reaction rates of Hg^0 and Hg^I oxidation. For example, OH-initiated Hg^0 oxidation has been recently re-assessed through computational chemistry (Dibble et al., 2020) that it can contribute one-third of the global Hg^{II} production in model simulations (Shah et al., 2021), yet this pathway has been overlooked in earlier models (Holmes et al., 2010; Horowitz et al., 2017; Saiz-Lopez et al., 2020). In addition, the rates of most oxidation reactions used in models are computationally derived and related experimental kinetic studies are scarce. A recent experimental study on the $Hg^IBr + NO_2$ reaction reports that the measured rate can be much slower than the computational results (Wu et al., 2020), indicating the need to update the chemical constraints in models based on laboratory studies.

On the other hand, the reduction of atmospheric Hg^I and Hg^{II} remains much less known despite its importance and necessity in global Hg model simulations. A general assumption is that the reduction proceeds mainly in the aqueous and gaseous phase, which often serves as a tuning model constraint to compensate for the fast oxidation process (Amos et al., 2012; Bash et al., 2014; Holmes et al., 2010; Horowitz et al., 2017; Saiz-Lopez et al., 2018; Selin et al., 2007; Shah et al., 2021, 2016). Recent models generally consider the main atmospheric Hg^{II} reduction process to be the aqueous-phase photolysis of either Hg^{II}-organic complexes in cloud droplets or Hg^{II}-organic aerosols (Horowitz et al., 2017; Shah et al., 2021, 2016). However, this assumption has been greatly challenged by the latest experimental studies in atmospheric waters and theoretical calculations on gas-phase reactions. Two recent experiments reported pseudo-first-order rate constants for Hg photoreduction in natural rainfall samples (Fu et al., 2021; Yang et al., 2019), and large discrepancies are found between the measured rates ($< 0.15\ hr^{-1}$) and those assumed in models ($\sim 1\ hr^{-1}$) (Saiz-Lopez et al., 2018). Rapid gas-phase photolysis and dark reduction reactions of Hg^{II} and Hg^I compounds are supported by recent theoretical calculations (Fig. 1) (Francés-Monerris et al., 2020; Khiri et al., 2020; Lam et al., 2019; Saiz-Lopez et al., 2019, 2018) yet with little experimental validation.

The transformations of atmospheric Hg are further complicated by redox reactions involving aerosols. Photoreduction of particulate Hg^{II} is reported in fly ash, $PM_{2.5}$, and soot particles (Deng et al., 2019; Huang et al., 2019, 2021, ; Tong et al., 2014), which is important in urban areas with high levels of aerosols. However, to fully understand the role of particulate Hg reduction in the dynamic atmosphere requires further knowledge of the heterogeneous chemistry at the air-aerosol or liquid-aerosol interface. Studies have shown that increasing aerosol water content may promote the rates of photoreduction of particulate Hg^{II} (Deng et al., 2019; Huang et al., 2021), whereas other studies suggest aqueous-phase Hg^{II} reduction can be inhibited upon the addition of fly ash into solutions (Feinberg et al., 2015). Previous studies report that particulate Hg accounts for more than 70% of total Hg found in cloud waters (Li et al., 2018; Weiss-Penzias et al., 2016), yet its chemical behavior is largely unknown and has been inadequately simulated in global Hg models.

A robust model simulation on atmospheric Hg not only depends on the knowledge of Hg redox chemistry but also requires a better characterization of the deposition mechanisms. For example, foliar uptake can partially explain the seasonal variations of Hg^0 at inland terrestrial sites (Fu et al., 2016; Jiskra et al., 2018), which cannot be reproduced in models by adjusting the extent of redox chemistry (Holmes et al., 2010; Horowitz et al., 2017). Furthermore, recent Hg isotope measurements suggest that Hg^0 contributes substantially ($>$ 50 %) to the surface ocean (Jiskra et al., 2021), challenging the current model simulations where Hg^{II} dominates the atmospheric deposition to the oceans (Horowitz et al., 2017; Shah et al., 2021).

So far, from the global Hg cycling and modeling perspective, the most critical knowledge gaps include:

1) **The chemical species of the oxidized Hg products.** Most atmospheric Hg speciation studies use an annular KCl denuder for the collection of gaseous oxidized mercury, potentially leading to an underestimation of the concentration and the loss of the original speciation information (Gustin et al., 2021). The development of better sampling and detection techniques is critically needed.
2) **Experimental kinetic studies.** Laboratory studies with focus on the photolysis of Hg^I and Hg^{II} compounds, $Hg^I + O_3/HO_2/NO_2$ oxidation reactions, and the chemistry of BrHgO radical under realistic atmospheric conditions are recommended and could provide valuable model constraints for atmospheric Hg redox chemistry. Photoreduction experiments with natural atmospheric waters, e.g., cloud water, from different locations and seasons are also needed. In addition to kinetic rate studies, future studies would benefit from Hg isotope measurements, organic

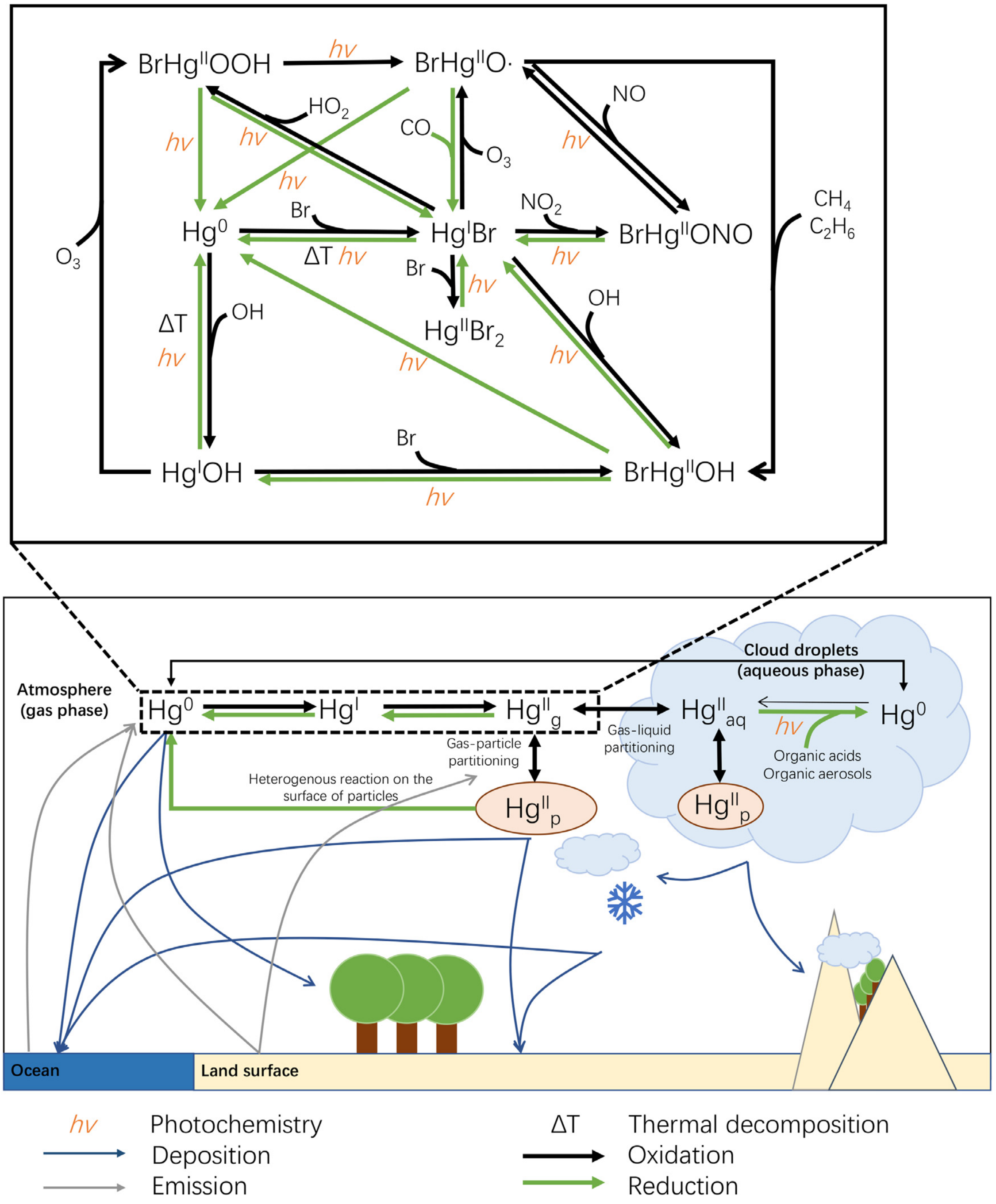

Fig. 1 – A schematic showing major Hg redox reactions in the atmosphere and deposition pathways (Ariya et al., 2015; Francés-Monerris et al., 2020; Goodsite et al., 2004; Holmes et al., 2006; Horowitz et al., 2017; Hynes et al., 2009; Jiskra et al., 2018; Khiri et al., 2020; Lam et al., 2019; Lohman et al., 2006; Obrist et al., 2021; Saiz-Lopez et al., 2020, 2019, 2018).

matter characterization in cloud water and aerosols, and oxidant, e.g., Br, monitoring with higher spatial and temporal resolutions.

3) **Heterogeneous Hg chemistry on aerosols.** Although fast photoreduction is observed with different atmospheric particles, the incorporation of such reduction pathway in models requires a better understanding of the Hg speciation on aerosols as well as the chemistry of particulate Hg in cloud waters.

4) **The linkage between theory, laboratory, and field campaigns.** Most experimental and theoretical studies are carried out under controlled conditions with concentrated reactants. The reactor differs greatly from the spatial-temporally dynamic environment and lacks the ability to reproduce meteorological conditions close to the real atmosphere, e.g., temperature, pressure, relative humidity, wind, and light regime. To reconcile such discrepancy, a wide range of atmospheric conditions in simulated

experimental and theoretical studies, or where possible mesocosm-scale studies should be considered.

3. Aqueous Hg transformations

Studies on mercury transformation in the aqueous environment often focus on the marine environment because humans and wildlife are exposed to Hg mainly by consuming seafood. Methylation is the major process that controls the levels of MeHg in the ocean, and it can occur via chemical and microbial pathways (Fig. 2). The microbial pathway dominates the methylation of Hg in the ocean (Blum et al., 2013; Ullrich et al., 2001). Monomethylmercury which is commonly referred to as MeHg has been commonly detected in both marine sediments (Azaroff et al., 2020; Hollweg et al., 2009) and seawater (Blum et al., 2013; Capo et al., 2020; Cossa et al., 2009; Lehnherr et al., 2011; Sunderland et al., 2009; Wang et al., 2018). There is no doubt that marine sediment is an important site for MeHg production, evidenced by both the detection of significant Hg methylation (Azaroff et al., 2020; Hollweg et al., 2009) and Hg methylation genes (*hgcAB*) (Yuan et al., 2019). However, the mechanism of MeHg enrichment in the subsurface ocean remains a subject of debate (Wang et al., 2018). The rates of Hg methylation measured in the open ocean water were relatively low and could also be caused by the artifact as suggested in a recent study (Wang et al., 2020a). In addition, *hgcAB* gene which is supposed to be necessary for Hg microbial methylation has not been detected in some open ocean systems (Bowman et al., 2020). In summary, the relative contributions of methylation in sediment and water to MeHg load in the water column of the open ocean remain unclear (Wang et al., 2018). However, recent isotope evidence suggested that MeHg in the biota of the deep sea may be mainly from the upper ocean, rather than the sediments, suggesting that there may be a pathway for MeHg production in the upper ocean (Sun et al., 2020a). Sampling campaigns in a variety of oceans showed that a subsurface MeHg enrichment layer appears to be ubiquitous in global oceans (AMAP/UNEP, 2018; Cossa et al., 2009; Lehnherr et al., 2011; Sunderland et al., 2009; Wang et al., 2018), which would arguably be the largest MeHg source for biological uptake/human exposure. This may be the major layer for MeHg production in the ocean; nevertheless, the mechanism of MeHg production in this layer has yet to be clear. As aforementioned, the *hgcAB* gene clusters are considered a reliable molecular marker to identify Hg methylating communities responsible for MeHg production. Although these genes have been widely detected in marine systems (Capo et al., 2022; Podar et al., 2015; Villar et al., 2020; Yuan et al., 2019), there is still a lack of knowledge on the relationship between these genes with Hg methylation in the natural environment.

Dimethylmercury is one of the main species of MeHg in seawater. It has been ubiquitously detected in deep ocean water and can be the major form of MeHg in the open ocean (Cossa et al., 1994; Kotnik et al., 2015; Lehnherr et al., 2011; Mason et al., 1995). The degradation of DMHg in seawater generates MeHg, which could serve as a potential source of MeHg in seawater (Mason et al., 1995). Several pathways have been proposed to produce DMHg in seawater, including the phytoplankton, microorganisms (Jonsson et al., 2016), and the reaction of hydrogen sulfide with MeHg (Rowland et al., 1977). Further studies are needed to explore the role of DMHg production in MeHg cycling and elucidate the mechanism for DMHg production in the ocean.

In the future, more efforts should be made on:

Identifying the ‘hot spots’ for MeHg production in the ocean. A variety of systems in the ocean may have the high efficiency of transforming IHg to MeHg, e.g., hydrothermal vent, subsurface layer with low oxygen level, cold seep, and trench. Methylation rates in these systems should be measured in the future to identify the ‘hot spots’ for MeHg production in the ocean as well as the mechanisms and controlling factors. This is crucial for evaluating the long-term risk of Hg in the ocean and comprehensively understanding the global Hg cycle.

4. Soil Hg transformations

Mercury undergoes redox transformation, methylation, and reduction in the terrestrial environment, affected by soil physicochemical properties. Compared with Hg^0, Hg^{II} is more commonly detected in soils. Elemental Hg is likely to be oxidated under aerobic conditions, especially in the presence of soil organic matter due to its role in complexing Hg^{II} as well as preventing Hg^{II} from being reduced (Windmoller et al., 2015). Microorganisms can also oxidize Hg^0 to Hg^{II} including the genera *Rhodanobacter* and diverse sulfate-reducing bacteria (SRB) including *Desulfobulbus, Desulfuromonas, Desulfomicrobium* (Huang et al., 2019a, b).

Both abiotic and biotic reduction of Hg^{II} occurs in soils. Organic acids predominantly influence the abiotic reduction of Hg^{II}. For instance, it has been shown that organic acids such as humic substances can reduce Hg^{II} to Hg^0 under abiotic dark conditions, and this process is mediated by the pH and salinity of the environment (Chakraborty et al., 2015). For biotic reduction, microorganisms are believed to partly contribute to soil Hg^0 emission by directly reducing Hg^{II} in soils (Fritsche et al., 2008). Hg-resistant microorganisms and Hg-sensitive metal-reducing bacteria are the two major contributors. The former is mediated by the reducing enzyme, i.e., *merA* mercuric reductase. For instance, a Hg-resistant bacterium *Sphingopyxis* sp. SE2 possessing the *mer*A gene could reduce IHg to Hg^0 with a maximum transformation efficiency of 44% (Mahbub et al., 2017). A similar phenomenon was observed in other genera such as *Pseudomonas, Bacillus*, and *Pseudoalteromonas* (Joshi et al., 2021). Besides *mer*-operon-mediated reduction, the phototrophic metal-reducing bacterium *Heliobacillus mobilis* has been proven to reduce Hg^{II} to Hg^0 by a mechanism different from the mercuric reductase (Lavoie et al., 2020).

Mercury methylation and demethylation in the soil environment are mainly biotic processes, although light-driven demethylation is also involved. Microbial methylation of inorganic Hg in the environment is the main pathway contributing to MeHg accumulation in environments (Driscoll et al., 2013; Pak and Bartha, 1998), which is driven by certain anaerobic microbes harboring *hgcAB* genes (Parks et al., 2013). The *hgcAB* gene clusters are considered a reliable molecular marker to identify Hg methylating communities responsible for MeHg production (Christensen et al., 2016). The reported *hgcAB* microbes are mainly distributed within phyla of Deltaproteobacteria, Chloroflexi, Firmicutes, and Euryarchaeota (i.e. *Methanomicrobia*), as well as Aminicenantes, Spirochaetes, and Kiritimatiellaeota (Gilmour et al., 2013; Jones et al., 2019; Lin et al., 2021). These potential Hg methylators have been detected in diverse habitats including sediments of ocean, lake, and mangrove, paddy soils, boreal forest soils, and Antarctic sea ice (Niu et al., 2021; Tang et al., 2020). Definitely, environmental variables such as the dissolved organic matter attributes and sulfur speciation are crucial determinants of Hg bioavailability and thus affect Hg methylation (Graham et al., 2017; Regnell and Watras, 2018). Particularly, the differences in the thiol-Hg complex would lead to their distinct bioavailability to environmental microorganisms (Liu et al., 2016; Song et al., 2018), which also rely on the species of microbial Hg methylator.

Regarding microbial demethylation, reductive demethylation and oxidative demethylation are the two main processes, distinguished by the products. The products of reductive demethylation are Hg^0 and methane, while the products of oxidative demethylation are Hg^{II}, carbon dioxide, and a small amount of methane (Lu et al., 2016; Oremland et al., 1991). Reductive demethylation often refers to mer-mediated demethylation, and the mechanism of methanotrophic demethylation is obscure (Barkay and Gu, 2022), although the iron-reducing bacterium *Geobacter bemidjiensis* Bem has also been shown to degrade MeHg via a reductive demethylation pathway (Lu et al., 2016). Mechanisms of oxidative demethylation remain obscure and are complicated by abiotic reactions via the formation of $(CH_3Hg)_2S$ intermediates in anoxic environments. Methanotrophs, such as *Methylosinus trichosporium* OB3b, also degrade MeHg utilizing a different demethylation pathway (Lu et al., 2017). Additional details of both biotic and abiotic demethylation can be found in a recent critical review by Barkay and Gu (2022).

Despite great progress in understanding Hg methylating microorganisms, we still lack a mechanistic understanding of MeHg production in real environments. Previous lab-based results have demonstrated huge differences in Hg methylation potential across different microbial species (Gilmour et al., 2013), which could be related to their different abilities to take up Hg and the activities of Hg methylating enzymes. It is thus imperative to ascertain the microbial diversity of the Hg methylating community in various environments we are concerned with (Liu et al., 2018). Such knowledge may help explain why we observe distinct MeHg production in the ecosystems with similar total Hg contents. Therefore, understanding how microbial cells take up Hg is fundamental to unraveling Hg methylation by diverse microbial species. Consequently, we could be able to apply these achievements in microbial Hg methylation to predict or mitigate MeHg risks in real environments, which requires detailed assessments of Hg content and speciation, the microbial communities involved in Hg methylation, as well as other abiotic factors associated with Hg bioavailability and microbial activity.

In the future, emphasis on soil Hg transformation should be addressed on the following aspects:

1) **Hg methylation under global change**: Mercury-contaminated ecosystems are also subject to global changes including climatic fluctuation and anthropogenic disturbances, which would likely change the condition associated with microbial Hg methylation. For example, extreme rainfall could lead to the formation of anoxic agricultural uplands and forest flooding, which may facilitate Hg methylation by anaerobic microorganisms. Meanwhile, attention should be paid to the potential changes in Hg methylation in response to global warming, under the circumstance of which both microbial activities and the availability of Hg could be impacted (Wang et al., 2020b; Zhang et al., 2021).

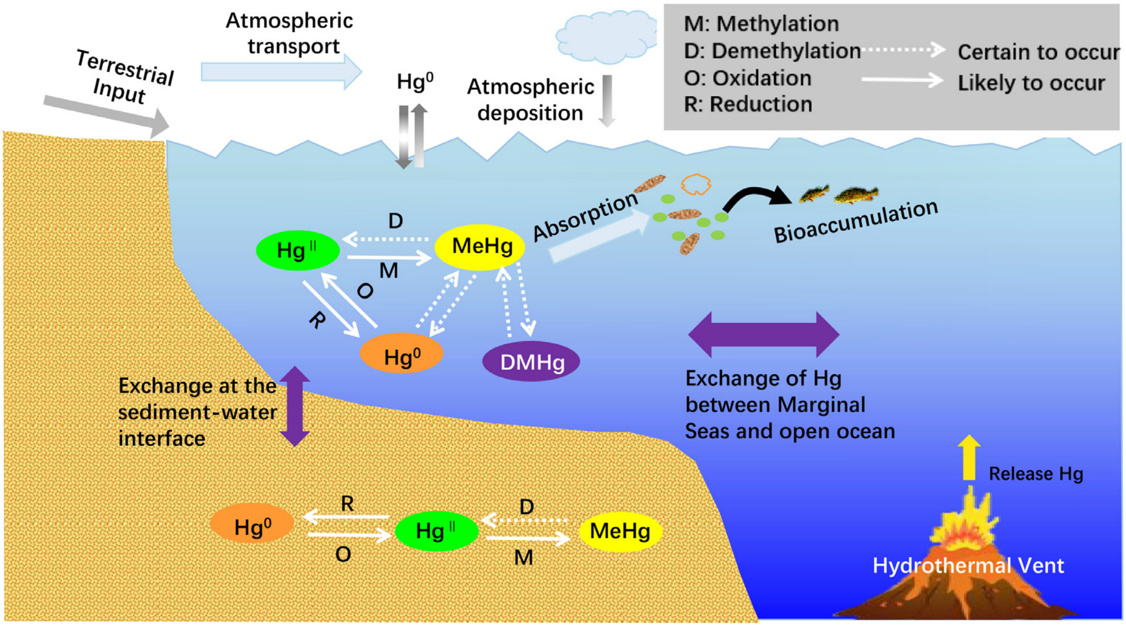

Fig. 2 – A schematic showing the cycling of Hg in the ocean.

2) **Identification of unknown microbial methylators**. Moreover, we note that our current understanding of microbes involved in Hg methylation is limited, and the identification of unknown species responsible for Hg methylation will underpin our knowledge of MeHg production in the real environment (Vigneron et al., 2021). Recent metagenomic analyses report some new potential Hg methylators in marine systems, which is an important step moving forward in our recognition.

5. Hg transformation by higher plants and organisms

Compared to Hg transformation in various environmental media, as summarized above, the processes within higher plants and organisms are poorly understood, except in microorganisms and under a few other situations. Hg transformations have been observed in animals, periphytons, and plants. Guts, livers, and brains are major organs for Hg transformation within animals (Kaschak et al., 2014; Ma et al., 2018; Renedo et al., 2021). Generally, gut microbes are the major driving force for the transformation of Hg in the gut environment. For example, SRB species detected in the gastrointestinal tract of aquatic organisms (e.g., fish) (Manceau et al., 2021), terrestrial invertebrates (e.g., earthworms) (Kaschak et al., 2014), and mammals (e.g., mice) (Singh et al., 2021) contribute to IHg methylation (Martín-Doimeadios et al., 2017). It has also been reported that MeHg demethylation occurs in the intestine of fish and mammals (Wang et al., 2017; Li et al., 2020). Livers and brains are the main organs for MeHg degradation. For instance, *in vivo* experiments exposing juvenile zebraseabreams to MeHg showed that the amount of MeHg was significantly reduced to 60% of the THg in the liver, and ~10% of MeHg was decreased in the brain (Branco et al., 2011). Periphytons are reported to methylate IHg, and Hg transformation within periphytons is probably achieved by microorganisms. For example, there is clear evidence showing that methanogens rather than SRB are the primary methylator of Hg in periphytic biofilms (Hamelin et al., 2011). Concerning higher plants, Hg transformation in rice plants (*Oryza sativa* L.) has received increasing attention. Currently, it is believed that the methylation of Hg would not occur in rice plants; however, demethylation of MeHg was observed when exposing rice plants to dissolved MeHg, although whether plant, ambient light, or microorganism (either rhizospheric or endophytic) drives the processes is unknown and the underlying mechanisms are to be explored (Xu et al., 2016; Strickman and Mitchell, 2017). Other higher plants may also be able to demethylate MeHg. For example, Maize (*Zea mays* L.) leaves could adsorb atmospheric Hg^0, and Hg methylation is likely to occur on the leaf surfaces (Sun et al., 2020b). It has also been found that maize grains might demethylate MeHg and release Hg^0 to the atmosphere, as a decrease of ~93-96% of MeHg and ~51%-73% of THg in maize grains has been observed (Sun et al., 2020b). In addition to demethylation, methylation has also been suspected to occur within higher plants. For instance, water spinach (*Ipomoea aquatica*) has been reported to methylate IHg *in vivo* (Göthberg and Greger, 2006).

However, as aforementioned, the transformation of Hg in intestines and periphytons is likely due to the role of microbes, and the mechanisms of Hg transformation processes observed in other organisms (e.g., higher plants) are still on debate and far from clear. Particularly, it is unknown whether those transformations could be attributed to microbial processes. For instance, in the studies of Xu et al. (2016) and Sun et al. (2020b), the authors did not reveal the demethylation mechanisms within plants and advocated further research. On the other hand, although Göthberg and Greger (2006) showed that water spinach could methylate IHg even under sterilized conditions, the role of endophytes has not been examined.

In addition to microbial processes, other possible mechanisms for Hg transformation *in vivo* have also been proposed but are to be confirmed. For example, Strickman and Mitchell (2017) speculated that the possible demethylation of MeHg by rice plants was probably attributed to photolysis because the demethylation rate was higher in illuminated shoots (~45%) compared with underground roots (~22%). Similarly, it has been reported that the marine microalga, *Isochrysis galbana*, could degrade MeHg within cells, and intracellular IHg was reduced as well (Kritee et al., 2018). The MeHg demethylation and Hg^{II} reduction were evidenced to result from visible light (Kritee et al., 2018). Besides, electrochemical mechanisms may be involved in Hg transformation in plants. A novel mechanism for plants reducing Hg^{II} to Hg^0 has been proposed by Battke et al. (2005), revealing a potential Hg metabolism pathway in plants. They suggested an electron transfer from nicotinamide adenine dinucleotide phosphate to Hg^{II} via glutathione and ascorbate acid. However, the role of microorganisms, either in the environment or within organisms, in biotic MeHg transformation has not been clarified in those previous studies.

In summary, we have just taken the first step in understanding the Hg transformation processes within organisms other than microbes, and one critical gap is:

Whether and how Hg transformation occurs within organisms. More studies are needed to confirm that Hg methylation/demethylation or Hg oxidation/reduction could happen *in vivo*, and potentially unknown mechanisms (other than microbial transformation and photodegradation) responsible for those processes are to be explored or tested. Particularly for plants, currently, it is unknown whether the *in vivo* processes or ambient microbes/light are responsible for the observed MeHg demethylation. These gaps have largely hindered our ability to predict Hg bioaccumulation in our food, the subsequent dietary exposure, as well as the associate health risk if we have a poor understanding of the transformation of Hg during the whole process of trophic transfer in human food webs.

6. Mercury isotope fractionations as a tool for tracing Hg transformation processes

Mercury stable isotopes have revolutionized our understanding of Hg transformations in many aspects, including some key processes in atmospheric, terrestrial, marine, and polar environments (Bergquist and Blum, 2009; Blum et al., 2014;

Kwon et al., 2020), and thus have now become an indispensable and irreplaceable approach for tracing the biogeochemical cycle of Hg. Mercury isotopes exhibit both mass-dependent fractionation (MDF) and mass-independent fractionation of odd (odd-MIF) and even mass number isotopes (even-MIF). This advantage makes Hg isotopes a unique "three-dimensional" tracer that permits differentiation between complex sources and transformations of Hg. The most important milestones in the research on Hg isotopes are the discovery of odd- and even-MIF (Bergquist and Blum, 2007; Gratz et al., 2010; Chen et al., 2012) in a wide variety of natural samples, e.g., animal tissues, atmospheric Hg, soils, plants, and sediments (Blum et al., 2014). It is now clear that the odd-MIF signals in natural samples are primarily produced by photochemical processes (e.g., photoreduction of Hg^{II} and photodegradation of methylmercury), as evidenced by multiple experimental studies (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009, 2010; Chandan et al., 2015; Kritee et al., 2018; Motta et al., 2020). The even-MIF is so far discovered in atmospheric Hg species and reservoirs that receive atmospheric Hg deposition, e.g., seawater, lake water, soils, and plants (Blum et al., 2014; Kwon et al., 2020), and was proposed to be driven by atmospheric (potentially gas phase) redox processes (Gratz et al., 2010; Chen et al., 2012; Cai and Chen, 2016; Fu et al., 2021), although the exact mechanism is still unclear.

Despite significant advances, substantial knowledge gaps still exist in both the fractionation mechanism and application of Hg isotopes in natural environments. Future efforts should dedicate to the following frontiers:

1) **The mechanisms of odd- and even-MIF.** The different types of MIF are closely linked to specific transformation processes. However, quantitative theoretical frameworks for both odd- and even-MIF are still lacking. A better theoretical understanding of the molecular-scale processes that give rise to MIF and experimental constraints on the direction, extent, and characteristics of MIF are necessary for the proper application of Hg MIF as a tracer of the Hg cycle.
2) **The isotope signature of Hg species and end-member sources.** Many important end-member sources have little Hg isotope data, including seawater, climate archives like ice core, coral, stalagmite, primary emission sources such as volcanic degassing, hydrothermal vents, and secondary emission sources such as re-emission from soils, water bodies, snow/ice, and biomass burning. These end-member sources typically have low levels of Hg, or it is challenging to collect and preconcentrate Hg from these samples for isotopic analysis. For example, the ocean is one of the largest reservoirs of Hg on the Earth's surface, but direct analysis of Hg isotopic compositions in seawater has been scarce due to the extremely low concentration and the high matrix interference of seawater. A recent study on Hg isotope compositions of seawater from the global ocean reveals a significant contribution of atmospheric Hg^0 to the marine Hg inventory ($>$50%) (Jiskra et al., 2021), challenging the traditional view that atmospheric Hg^{II} is the dominant Hg form that deposits to the ocean, and highlighting the need to better characterize the isotope compositions of seawater and fractionation processes during Hg transformation in the ocean. In addition, the isotopic compositions of different Hg species in these end-member sources (e.g., inorganic Hg vs. MeHg in the ocean, or Hg^0 vs. Hg^{II} in the atmosphere) are also critical for a better understanding of the transformation of Hg in the environment. Although studies on the species-specific Hg isotope analysis have been increasing in recent years, the techniques to separate different Hg species and obtain high-precision isotope data for them are still challenging. Therefore, more efforts on this front are still needed to further expand the application of Hg isotopes.
3) **The fractionation of Hg isotopes during transformation processes in natural environments.** In the atmospheric environment, the isotopic compositions of various atmospheric Hg species have been increasingly characterized, but the driving forces for the isotope fractionation between these species are poorly understood. For example, atmospheric redox reactions between Hg^{II} and Hg^0 are hypothesized to produce even-MIF, and thus quantification of Hg isotope fractionation during these processes is crucial for the application of even-MIF as a reliable tracer (Cai and Chen, 2016; Fu et al., 2021). In the marine environment, the detection of MIF in biological tissues has provided key evidence for tracing the biological uptake and trophic transfer of MeHg in the marine food web, as well as the production and photodegradation of MeHg in seawater (Bergquist and Blum, 2007; Blum et al., 2013). However, neither the fractionations during transformations within seawater and inside living organisms are well understood. In the terrestrial environment, the application of Hg isotopes has led to one of the most important breakthroughs in the terrestrial Hg cycle—the recognition of the importance of atmospheric Hg^0 uptake by vegetation and its subsequent incorporation into soils as a major global sink of Hg (Demers et al., 2013; Zheng et al., 2016; Obrist et al., 2018; Yuan et al., 2019; Wang et al., 2021). However, knowledge on how Hg isotopes fractionate during transformations within soils and during re-emission from soils and vegetation, which is crucial for tracing the transport of Hg from terrestrial to other ecosystems, is still lacking (Zhu et al., 2021). In the polar environment, Hg transformations are different from those at lower latitudes due to the unique climate and chemical processes. For example, the intense oxidation of atmospheric Hg^0 and photochemical re-emission from snow in polar spring have long been considered as the key processes controlling Hg accumulation in snow/ice and potentially in the polar ecosystem (Durnford and Dastoor, 2011), but studies on Hg isotope fractionation during these processes are very limited (Sherman et al., 2010; Obrist et al., 2017; Zheng et al., 2021). Future application of Hg isotopes in tracing the polar Hg cycle requires more efforts in characterizing Hg isotope fractionation during these processes. At last, in recent years, Hg isotopes have attracted a lot of attention as an emerging proxy for paleoenvironmental changes, e.g., volcanism and ocean redox evolution, (Grasby et al., 2019), which are often linked to critical biological evolution in Earth's history. Thus, more efforts are also needed to better characterize Hg isotope fractionation during transformation processes that are pertinent to the Hg cycle in the paleoenvironment.

4) **Isotope-based numeric models for Hg cycling.** Adding Hg isotopes into the current models of the Hg cycling would provide additional, independent constraints on the simulated processes and fluxes of Hg between reservoirs, as these processes and fluxes must satisfy the isotopic mass balance. Recent applications of such Hg isotope box models have enabled us to re-evaluate some key processes in the global Hg cycle, such as the fluxes of terrestrial Hg re-emission (Sonke, 2011; Sun et al., 2019). A better constraint on the global Hg cycle would benefit from more efforts in the integration of Hg isotope fractionation data obtained from observational, experimental, and theoretical studies into numeric models.

7. Perspectives and recommendations

Understanding and solving Hg pollution problems call for global efforts and cooperation. Although Hg is an “old” pollutant that has been studied for decades, many key processes and mechanisms regarding environmental chemistry and health risks of Hg remain unsolved. Herein, we discussed the methodologies for exploring Hg transformations both in the environmental media and within organisms. In filling the knowledge gap of Hg transformations, special attention should be paid to at least the following:

1) Incorporate the processes and mechanisms into realistic environmental conditions and scenarios, and elucidate the importance of these processes and mechanisms from the perspective of local, regional, and global scales. Simulated environmental scenarios and quantitative reaction parameters would facilitate the linking between field and laboratory observations.
2) Better integrate the environmental processes and mechanisms of Hg with mechanistic models, further guide remediation and adaption strategies, and support policymaking to ultimately improve environmental and human health.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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