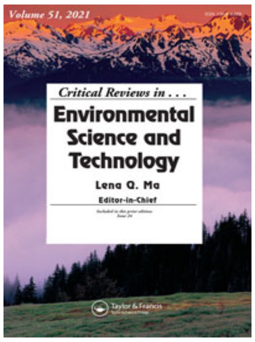

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ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/best20

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To cite this article: Kang Wang, Guangliang Liu & Yong Cai (2021): Possible pathways for mercury methylation in oxic marine waters, Critical Reviews in Environmental Science and Technology, DOI: 10.1080/10643389.2021.2008753

To link to this article: https://doi.org/10.1080/10643389.2021.2008753

CRITICAL REVIEWS IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY
https://doi.org/10.1080/10643389.2021.2008753

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INVITED REVIEW

Possible pathways for mercury methylation in oxic marine waters

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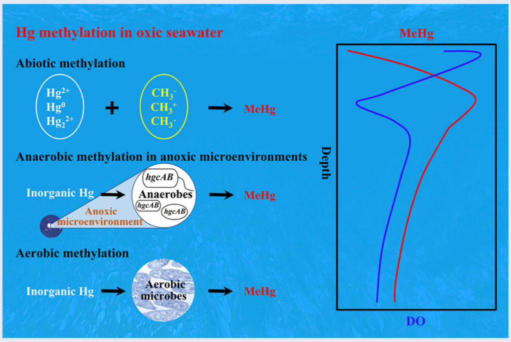
ABSTRACT



Mercury (Hg) is a global contaminant that presents public health risks through seafood consumption primarily in the form of monomethylmercury (MMHg). Methylation of inorganic Hg in water column has been considered a major source of seawater MMHg, but the known Hg methylation by anaerobes possessing the hgcAB gene cluster in anoxic environments could not directly explain the formation and widespread presence of MMHg in seawater where oxic conditions are usually present. In this review, we synthesized the information on previously reported possible pathways to explain the Hg methylation in oxic marine waters, including Hg methylation by (1) methyl donors like organic compounds and organometallic complexes in seawater via abiotic pathways, (2) anaerobic microbes in anoxic microenvironments within oxic seawater, and (3) aerobic microbes in oxic seawater. We evaluated the potential contributions of respective Hg methylation pathways to MMHg in seawaters and discussed the perspectives on future research needs for an improved understanding of seawater Hg methylation. We inferred that while all proposed Hg methylation pathways remain to be further verified, at least one and maybe all of them are plausible depending on ocean conditions. Development and application of new techniques, e.g., quantifying Hg isotope fractionation, would help differentiate (e.g., abiotic versus biotic) Hg methylation pathways. Comprehensive studies toward bridging the gaps between microbial gene screening and Hg methylating capability, between Hg methylation incubation and field MMHg measurement, and between mechanistic Hg methylation studies and environmental relevance will benefit the elucidation of Hg methylation pathways and MMHg distribution in seawater.

KEYWORDS Abiotic mercury methylation; aerobic mercury methylation; anaerobic mercury methylation; anoxic microenvironments; Mercury methylation; oxic seawater

HANDLING EDITORS Jörg Rinklebe and Lena Ma

1. Introduction

Mercury (Hg) is a pollutant with global concern, due to its high toxicity and bioaccumulation, especially in the form of monomethylmercury (MMHg), in food webs (Selin, 2009). Anthropogenic activities have raised Hg levels in the biosphere by at least three times since industrial revolution (Mason et al., 2012). Humans are exposed to MMHg primarily through the

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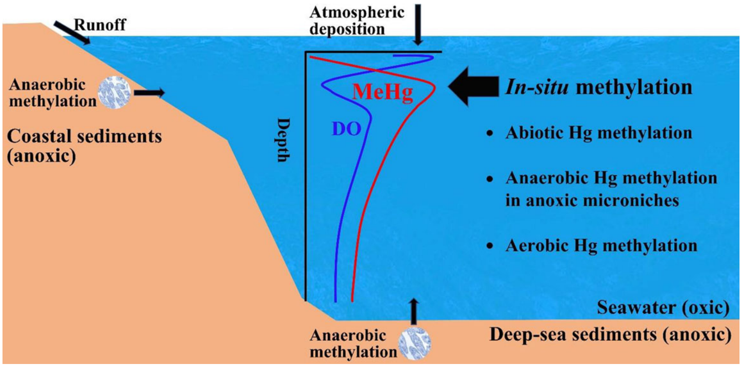

Figure 1. Typical vertical profiles of methylated mercury (MeHg) and dissolved oxygen (DO) in marine waters and potential sources of seawater MeHg, with *in-situ* methylation being the major while runoff, atmospheric deposition, and sediment production minor sources.

consumption of marine products, except in certain heavily contaminated inland areas (Lavoie et al., 2018; Sunderland, 2007; Zhang et al., 2010). Seawater Hg species are the principal sources of MMHg in marine animals (Atwell et al., 1998; Schartup et al., 2018). Different than in marine fish where most of the Hg exists as MMHg (Agah et al., 2007; Park et al., 2011; Zhang et al., 2020), in marine waters this bioaccumulating Hg species accounts for a much smaller fraction of total Hg (Hg_T) (Bowman et al., 2020a). Inorganic Hg species, including divalent inorganic Hg (Hg^{2+}) and elemental Hg (Hg^0), consist the majority of Hg in seawater (Munson et al., 2015). Dimethylmercury (DMHg), an additional mercury species which is largely unique to seawater and can reach concentrations similar to or even higher than those of MMHg (Bowman et al., 2015; 2016; Kirk et al., 2008; Mason & Fitzgerald, 1993; Munson et al., 2015), has drawn great attention in recent years. Due to their interconversion in seawater, MMHg and DMHg are often not differentiated in seawater Hg data sets but reported in sum as methylated Hg (MeHg) (Cossa et al., 2009; 2011; Mason et al., 2012; Sunderland et al., 2009). Generally, MeHg composes no more than 20% of seawater Hg_T in the world oceans, although this percentage may reach more than 50% at certain depths in some regions (Bowman et al., 2020a).

The concentrations of MeHg measured from world oceans generally show a distinct vertical profile of MeHg along the depth in the water column, where maxima are usually observed in subsurface waters with decreased concentrations in surface and deeper waters (Figure 1) (Cossa et al., 2009; Heimbürger et al., 2015; Mason & Fitzgerald, 1990; Munson et al., 2015; Sunderland et al., 2009). The profile of MeHg is loosely related to that of dissolved oxygen (DO), with the peak concentrations of seawater MeHg typically in low oxygen waters. Although the specific depths at which MeHg and DO peak vary from ocean to ocean and from a region to another in the same ocean, the general patterns of MeHg and DO distribution in the water column appear intriguing with regard to examining the sources of MeHg in ocean waters.

There are multiple external and internal sources contributing to seawater MeHg, but their relative importance remains a subject of debate. Globally, direct atmospheric deposition and riverine transport are considered minor sources for oceanic MeHg (Liu et al., 2021; Mason et al., 2012). Earlier studies suggest that marine MeHg is mainly supplied by its production in anoxic coastal sediments and subsequent release to the overlying seawater (Hammerschmidt & Fitzgerald, 2006; Kraepiel et al., 2003). However, if MeHg in seawater has a short life time as suggested by incubation studies (Lehnherr et al., 2011; Monperrus et al., 2007; Whalin et al., 2007), the MeHg produced from coastal sediments can hardly make its way to the open ocean (Cossa et al., 2017). MeHg production in anoxic deep-sea sediments, although not well documented, could act as a possible source of MeHg in the open ocean (Kraepiel et al., 2003). However, this source cannot explain the observed MeHg profiles, i.e., lower concentrations in deeper waters beneath the maxima in subsurface waters (Cossa et al., 2009; Heimbürger et al., 2015; Mason & Fitzgerald, 1990; Munson et al., 2015; Sunderland et al., 2009).

Considering the insignificance of external sources, *in-situ* methylation of inorganic Hg in the water column has increasingly prevailed as the major source of seawater MeHg (Lehnherr, 2014; Mason et al., 2012). Many incubation studies have observed the methylation of isotopically labeled inorganic Hg^{2+} added in seawater (Lehnherr et al., 2011; Monperrus et al., 2007; Munson et al., 2018). The major role of *in-situ* Hg methylation in forming seawater MeHg and MMHg has been inferred from mass budget calculations for the Pacific (Kim et al., 2017) and Arctic Oceans (Soerensen et al., 2016). The Hg isotope composition in marine biota evidenced that the biotic MMHg mainly originated from Hg methylation in water column (Blum et al., 2013; Li et al., 2016; Sun et al., 2020). More importantly, the MeHg profile and its association with DO appear to be consistent with *in-situ* Hg methylation being the primary MeHg source in ocean waters. The enrichment of MeHg occurs in low oxygen waters, where heterotrophic microorganisms respire sinking organic matter (OM). This agrees with the correlations between MeHg concentrations and remineralization proxies such as apparent oxygen utilization observed in a vast majority of literature studying MeHg in the world oceans, suggesting an association between Hg methylation and heterotrophic OM remineralization (Bowman et al., 2016; Cossa et al., 2009; 2011; Heimbürger et al., 2010; Kim et al., 2017; Munson et al., 2015; Sunderland et al., 2009; Wang et al., 2012). In some oligotrophic regions, however, no significant correlations were found between MeHg and microbial respiration proxies (Agather et al., 2019; Bowman et al., 2015). Although less frequent, in some cases MeHg maxima were observed at subsurface chlorophyll maximum in oxygenated euphotic zone (Bowman et al., 2015; 2016; Bratkič et al., 2016; Wang et al., 2018). The MeHg enrichment in euphotic zone suggests an association between Hg methylation and primary production, probably by providing OM that stimulate heterotrophic microbial activities and accompanying Hg methylation (Heimbürger et al., 2010). Meanwhile, inorganic Hg^{2+} is transported by settling OM from euphotic zone to deeper waters and serves as substrate for Hg methylation by heterotrophic activities (Sunderland et al., 2009). During the heterotrophic respiration, MMHg bound on OM is also released in low oxygen waters, but estimates show that this source is of minor contribution (Cossa et al., 2009).

Assuming *in-situ* Hg methylation in the water column to be the principal source of seawater MeHg, the next question to be asked would be through what mechanisms inorganic Hg is methylated in seawater. In general, Hg methylation by anaerobic microbes such as sulfate- and iron-reducing bacteria (Compeau & Bartha, 1985; Kerin et al., 2006) has been considered the primary source of MMHg in aquatic environments (Ullrich et al., 2001). The recently revealed mechanism (Parks et al., 2013) showed that the *hgcA* and *hgcB* genes and their encoding proteins are responsible for Hg methylation by anaerobic bacteria and archaea. The *hgcA* gene encodes a putative corrinoid protein (HgcA) capable of transferring a methyl group to inorganic Hg^{2+}; the *hgcB* gene encodes a 2[4Fe-4S] ferredoxin (HgcB) that reduces HgcA to a state that enables it to receive a new methyl group (Figure 2) (Parks et al., 2013). Redox potential is among the biogeochemical factors that affect the *hgcAB*-mediated Hg methylation (Beckers et al., 2019; Frohne et al., 2012; Wang et al., 2021) by regulating the activities of Hg methylators and/or their uptake of inorganic Hg (Ma et al., 2019; Regnell & Watras, 2019). Given the peak concentrations of seawater MeHg in low oxygen waters and their association with heterotrophic microbial activities, anaerobic microbial Hg methylation involving *hgcAB* gene cluster has been postulated to be responsible for water column Hg methylation in seawater (Bowman et al., 2020b).

However, anaerobic microbial Hg methylation cannot directly explain Hg methylation *in-situ* in seawater column. Although DO is low in subsurface waters with MeHg enrichment (Mason et al., 2012), anoxic conditions are hardly reached, except in some coastal waters, the Black Sea and brackish Baltic Sea (Kuss et al., 2017; Lamborg et al., 2008; Pakhomova et al., 2014; Rosati et al., 2018). Even in the low oxygen waters of Eastern Equatorial Pacific and Northern Indian

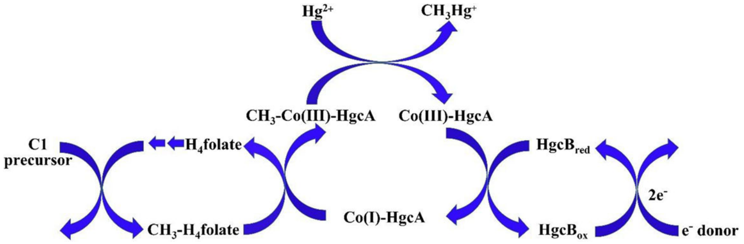

Figure 2. Schematic showing processes of Hg methylation mediated by activities of anaerobic microbes carrying *hgcAB* gene cluster.

Ocean where DO is $<5\,\mu$M, no evidence were found for the predominance of anaerobes capable of methylating Hg (Malcolm et al., 2010). Therefore, known anaerobic Hg methylators (i.e., those possessing *hgcA* and *hgcB* genes) are unlikely to thrive and produce MeHg in oxic marine waters. In reviewing previous studies to address the issue of Hg methylation in oxic seawaters, we classified the previously reported (or proposed) Hg methylation processes into three pathways: (1) Hg methylation by abiotic processes in seawater, (2) Hg methylation by anaerobic microbes in anoxic microenvironments within oxic seawater, and (3) Hg methylation by aerobic microbes in oxic seawater. These are the dominant pathways discussed in previous studies in attempting to explain the *in-situ* Hg methylation in oxic marine waters. The purpose of this review is to summarize the current understanding toward these water column Hg methylation pathways and discuss the knowledge gaps as well as perspectives on potential future research directions.

2. Abiotic mercury methylation

Inorganic Hg can be methylated in abiotic pathways if suitable methyl donors are present (Celo et al., 2006; Ullrich et al., 2001). Depending on whether irradiation is required, abiotic Hg methylation is divided into photochemical and non-photochemical methylation (Li & Cai, 2013). As a possible pathway for Hg methylation in oxic seawater (Podar et al., 2015; Regnell & Watras, 2019), abiotic Hg methylation is at least partially responsible for MeHg in marine waters (Lehnherr et al., 2011; Monperrus et al., 2007; Munson et al., 2018). Methylation of isotope-enriched inorganic Hg^{2+} spikes was observed in filtered (0.2 μm) marine waters of the central Pacific Ocean, and the methylation rates (1.5×10^{-2} d^{-1}) were higher than in unfiltered seawater (0.9×10^{-2} d^{-1}) (Munson et al., 2018). Unlike the typically used 0.45 μm filters that allow the passage of many microbes, 0.2 μm filters remove most organisms and greatly decrease the likelihood of microbial Hg methylation in filtered water. Therefore, the enhanced Hg methylation in filtered seawater was most likely attributed to abiotic mechanisms, instead of microbial Hg methylation which required the processes of dormant cells reactivation and rapid growth, and/or the preferential selection of Hg methylating cells by filtration (Munson et al., 2018). In addition, incubation studies often found substantial methylation of Hg at or immediately after the addition of isotopically labeled inorganic Hg (Lehnherr et al., 2011; Munson, 2014; Munson et al., 2018), which could only be explained by abiotic mechanisms but not microbial Hg methylation (Wang et al., 2020). The role of abiotic Hg methylation in marine waters was also supported by a recent study modeling global oceanic Hg, in which the MeHg concentrations in the Arctic Ocean and Southern Ocean were substantially underestimated due to not considering abiotic Hg methylation (Semeniuk & Dastoor, 2017).

During abiotic methylation process, methyl group is transferred from donor to acceptor in the form of carbocation (CH_3^+), carbanion (CH_3^-) or radical ($CH_3\bullet$), as described by Eq. (1) through (4) (Krishnamurthy, 1992). As shown by Eq. (1), methylation of Hg^{2+} can be fulfilled by transfer of CH_3^- but not CH_3^+, the acceptor of which should be oxidizable whereas Hg^{2+} is the

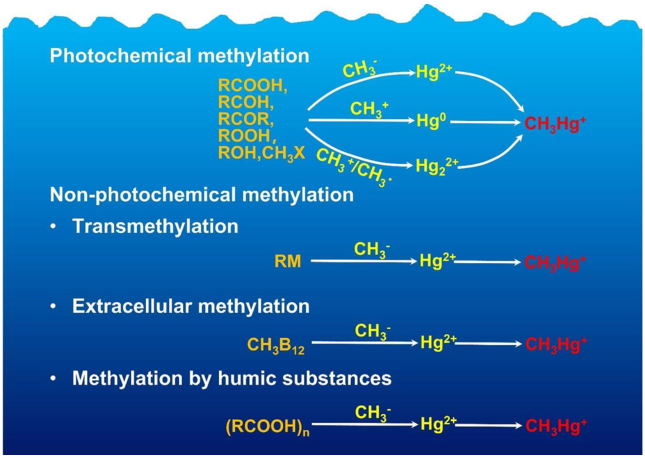

Figure 3. Major abiotic Hg methylation pathways in oxic waters. Methyl donors in photochemical Hg methylation may include methyl halides (CH_3X) and low molecular weight organic compounds such as organic acids (RCOOH), aldehydes (RCOH), ketones (RCOR), hydroperoxide (ROOH), and alcohols (ROH). Non-photochemical pathways include organometallic complexes (RM)-involved transmethylation, extracellular methylcobalamin (CH_3B_{12})-mediated Hg methylation, and Hg methylation by humic substances ($(RCOOH)_n$).

highest stable oxidation state of Hg (Weber, 1993). Meanwhile, the transfer of $CH_3{}^+$ to Hg^0 (Yin et al., 2014) and $Hg_2{}^{2+}$ may also methylate inorganic Hg (Weber, 1993), as described by Eqs. (2) and (3), respectively. Eq. (4) shows another pathway of Hg methylation that involves the transfer of $CH_3\bullet$ to $Hg_2{}^{2+}$ (Yin et al., 2014). Among these reactions, transfer of $CH_3{}^-$ to Hg^{2+} is considered the most plausible mechanism for abiotic Hg methylation (Chen et al., 2007; Weber, 1993; Yin et al., 2012). While $CH_3\bullet$ has been thought important for abiotic Hg methylation by many methyl donors (i.e., acetic acid, aldehydes, dimethylsufoxide, ketone, methylcobalamin) (Malinovsky & Vanhaecke, 2011; Yin et al., 2012), only methylation of $Hg_2{}^{2+}$ by $CH_3\bullet$ from methyl iodide (CH_3I) has been confirmed by experiments (Yin et al., 2014). The authors also verified the abiotic methylation of Hg^0 by $CH_3{}^+$ from CH_3I.

$$CH_3{}^- + Hg^{2+} \rightarrow CH_3Hg^+ \quad (1)$$

$$CH_3{}^+ + Hg^0 \rightarrow CH_3Hg^+ \quad (2)$$

$$CH_3{}^+ + Hg_2{}^{2+} \rightarrow CH_3Hg^+ + Hg^{2+} \quad (3)$$

$$CH_3 \bullet + \S Hg_2{}^{2+} \rightarrow CH_3Hg^+ \quad (4)$$

Photochemical Hg methylation starts from the photosensitization of methyl donors (Figure 3), mainly including low molecular weight organic compounds (LMWOCs, e.g., low molecular weight organic acids, aldehydes, ketones, peroxides, and alcohols) and methyl halides (especially CH_3I) (Akagi et al., 1972; Akagi & Sakagami, 1972; Yin et al., 2012; 2014). Although various LMWOCs are known to generate $CH_3\bullet$ under irradiation (Kaise et al., 1994), Hg methylation by free methyl radicals is unlikely a major pathway for photochemical methylation (Yin et al., 2012) except for CH_3I-involved methylation (Yin et al., 2014). Three steps are involved in the CH_3I-invloved methylation: (1) reduction of Hg^{2+} to Hg^0 and $Hg_2{}^{2+}$; (2) decomposition of CH_3I to $CH_3{}^+/I^-$ or $CH_3\bullet/I\bullet$ under irradiation; and (3) methylation of Hg^0 and $Hg_2{}^{2+}$ by $CH_3{}^+$ and $CH_3\bullet$, respectively. While CH_3I-assisted Hg methylation is an example with verified environmental occurrence, other methyl halide (e.g., methyl bromide) can also methylate Hg in similar mechanisms (Boynton & Taylor, 1954), although their occurrence in environments has not been observed. Non-photochemical Hg methylation include transmethylation that involves organometallic complexes as methyl donors (Cerrati et al., 1992; Howell et al., 1986; Jewett et al., 1978), extracellular Hg methylation by biogenetic methyl donors released to environments (DeSimone et al., 1973; Neujahr & Bertilsson, 1971), and Hg methylation by humic substances (Nagase et al., 1982, 1984; Weber et al., 1985). A variety of organometallic compounds have been shown to be able to methylate Hg, but except for methyltin compounds (Celo et al., 2006), transmethylation pathways are deemed environmentally insignificance for various reasons. For instance, methylarsenic compounds are not effective methyl donors (Chau et al., 1987); methyllead compounds in natural environments are in low concentrations (Radojevic & Harrison, 1987); effective Hg methylation by silicone compounds requires strict conditions such as high reaction temperature (>60 °C for methylation by hexamethyldisiloxane) or extremely high ignition temperature (500–700 °C for methylation by silicone gum) (Nagase et al., 1988). Extracellular Hg methylation refers primarily to the nonenzymatical Hg methylation by methylcobalamin (DeSimone et al., 1973; Neujahr & Bertilsson, 1971), to distinguish it from the *hgcAB*-mediated intracellular Hg methylation that also involves methylcobalamin (Parks et al., 2013). Extracellular Hg methylation usually proceeds through transfer of CH_3^- to Hg^{2+} (Chen et al., 2007), although methylcobalamin could also provide CH_3^+ or CH_3• (Banerjee & Ragsdale, 2003). Humic substances can serve as effective methyl donors for chemical Hg methylation, as evidenced by abiotic methylation of inorganic Hg by humic acid and fuvic acid derived from leaf mold, river sediment and soil under dark (Nagase et al., 1982, 1984; Weber et al., 1985). Only a few Hg-methylating compounds (e.g., 2, 6-di-tert.-butyl-4-methylphenol, *p*-xylene, mesitylene, and coniferol) have been identified inside humic substances, and our knowledge on Hg methylation by these compounds are very limited (Falter, 1999; Nagase et al., 1984). For the Hg methylation by humic substances, transfer of CH_3^- to Hg^{2+} is considered the dominant methylation pathway, although the methyl group donated to inorganic Hg remains unknown (Weber, 1993).

To gain more insights on corresponding abiotic Hg methylation in seawater, here we discuss the potential contributions of different abiotic Hg methylation in forming MeHg in marine environments. Although previous studies suggested the importance of OM-driven photochemical Hg methylation in producing MeHg in wet deposition and some lakes (Gårdfeldt et al., 2003; Hammerschmidt et al., 2007; Siciliano et al., 2005) and of CH_3I-induced photochemical Hg methylation in certain aquatic environments where CH_3I is present at concentrations (sub mM levels) (Celo et al., 2006; Yin et al., 2014) orders of magnitude higher than in seawater (pM levels) (Grose et al., 2007; Lovelock, 1975; Moore & Groszko, 1999), photochemical Hg methylation is unlikely an importance source of MeHg in marine waters. This notion is backed by the observed overall low MeHg concentrations in euphotic zone across the world oceans due to photodemethylation (Mason et al., 2012). For non-photochemical pathway, we evaluate the contribution of Hg methylation by methyltin compounds, as the roles of other methyl donors are likely limited. A previous estimation suggests that Hg methylation by methyltin compounds plays an important role in forming MeHg in marine environments (Celo et al., 2006). However, the monomethyltin concentrations used (∼10 nM) are among the highest values measured in seawater. Applying a more realistic monomethyltin concentration of 10 pM in seawater (Braman & Tompkins, 1979; Byrd & Andreae, 1982) would generate a pseudo-first-order (to inorganic Hg^{2+}) methylation rate constant of $5.0 \times 10^{-7}\ d^{-1}$, which is three orders of magnitude lower than that estimated from spatial distribution of Hg species in the Atlantic Ocean ($2.0 \times 10^{-4}\ d^{-1}$) (Mason et al., 1995). This implies that abiotic Hg methylation by methyltin compounds is not an important source of MeHg in seawater. For extracellular Hg methylation by methylcobalamin, Celo et al. (2006) observed the inhibiting effects of Cl^- and concluded that methylcobalamin was unlikely to methylate inorganic Hg^{2+} abiotically in moderately and highly saline environments. On the contrary, Jiménez-Moreno et al. (2013) and Chen et al. (2007) observed the abiotic methylation of inorganic Hg^{2+} by methylcobalamin in the presence of Cl^- at concentrations as high as 0.5 and 1.0 M, respectively. Both studies proposed that this Hg methylation might be of importance in marine environments. However, the reaction rates were obtained at lower pH (4 and 5) than that of marine waters (∼8). A quantitative estimate on the contribution is therefore hindered due to the lack of reaction rates at pH conditions more relevant to marine environments. For humic substances-mediated chemical Hg methylation, it is premature to quantitatively estimate its contribution to MeHg in marine waters, due to the varying composition of humic substances, different reaction kinetics depending on compounds/moieties involved in Hg methylation (Nagase et al., 1982, 1984; Weber et al., 1985), and lack of understanding on Hg methylation by specific methyl donors inside humic substances. Overall, while it is difficult to estimate the contribution of abiotic Hg methylation to seawater MeHg, previous studies have suggested that Hg methylation by methylcobalamin and humic substances might be important in marine waters (Munson et al., 2018; Semeniuk & Dastoor, 2017). Although the methyl donors responsible for seawater abiotic Hg methylation remain unclear, they are likely biogenic so the abiotic Hg methylation as an important source of seawater MeHg would not contradict the association observed between MeHg and biological activities, including both autotrophic (Bowman et al., 2015; Bratkič et al., 2018; Heimbürger et al., 2010) and heterotrophic activities (Cossa et al., 2009; Sunderland et al., 2009).

To quantify the contribution of abiotic Hg methylation in forming MeHg in seawater, we need to keep investigating abiotic Hg methylation by different compounds, which largely relies on development and improvement of techniques and methodologies in studying Hg methylation and demethylation. Much of our knowledge in abiotic Hg methylation was gained from studies in 1970–1990s, whereas less research is looking at abiotic Hg methylation in contemporary times (Beckers & Rinklebe, 2017). One major challenge is to delineate abiotic methylation from biotic methylation as it is difficult to sterilize environment samples (e.g., seawater) without changing their physical and chemical properties (Beckers & Rinklebe, 2017). While the difficulties of delicate sterilization persist, it is now possible to distinguish abiotic methylation from biotic methylation in environments like marine waters by using the techniques quantifying Hg isotope fractionation. Previous studies have found that Hg methylation and demethylation via different pathways result in different mass-dependent fractionation (MDF) and/or mass-independent fraction (MIF) signatures (Tsui et al., 2020). For example, Hg isotopes exhibited MDF with $^{202/198}\alpha_{\text{reactant/product}}$ at 1.0013–1.0020 and MIF with $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg} = 1.36 \pm 0.02$ (2SE) through photoreduction of MeHg (Bergquist & Blum, 2007); MDF of Hg isotopes with $^{202/198}\alpha_{\text{reactant/product}}$ of 1.0009 and 1.0011 was observed through anaerobic methylation by *Geobacter sulfurreducens* PCA and *Desulfovibrio desulfuricans* ND132, respectively (Janssen et al., 2016); isotopes of Hg showed MDF with $^{202/198}\alpha_{\text{reactant/product}}$ of 1.0005–1.0015 through abiotic methylation under dark by methylcobalamin, methytin, acetic acid and dimethylsufoxide (Malinovsky & Vanhaecke, 2011). This makes it possible to trace and quantify the sources of MeHg in environment samples (e.g., seawater) with their isotopic composition. However, the application is still premature due to: (1) its dependence on accurately and fully characterizing the MDF and MIF of Hg isotopes through different methylation and demethylation processes, and (2) analytical challenge resulting from the low concentrations of Hg species (particularly MeHg) in marine waters. While overcoming the first challenge relies on more studies characterizing Hg isotopes fractionations through methylation and demethylation processes in different pathways (Kritee et al., 2013), the second challenge can be addressed by development of techniques pre-concentrating Hg species from environment samples (Rosera et al., 2020).

As for the methodologies in studying Hg methylation and demethylation in seawater, currently one major approach is seawater incubation with additions of isotopically labeled Hg species (Wang et al., 2020). To investigate mechanisms or controlling factors of Hg reactions, certain treatments (e.g., sterilization) or amendments with certain cofactors (e.g., methylcobalamin) or inhibitors (e.g., molybdate to inhibit sulfate reducing metabolism) can be introduced in such incubation experiments (Munson et al., 2018). However, this approach has major deficiencies in investigating Hg methylation and demethylation in seawater (Wang et al., 2020). These reaction rates measured by this approach (Lehnherr et al., 2011; Monperrus et al., 2007; Munson et al.,

2018) are several orders of magnitude higher than those estimated from Hg species distribution in oceans (Mason et al., 1995). Meanwhile, unexplainable methylation and demethylation immediately after Hg addition are frequently observed in such incubation experiments (Wang et al., 2020). Both deficiencies are likely resulted from differences between incubations and *in-situ* environments. Such incubation experiments are usually carried out in ship-based or onshore laboratory with seawater collected from field. During the process conditions like pressure and chemical compositions (e.g., gases) alter from *in-situ* environments. When seawater is transported from *in-situ* environments to surface, pressure drops substantially (e.g., from ∼11 atm at the depth of 100 m to 1 atm at surface) and that leads to decreasing in concentrations of gases dissolved in seawater (e.g., CO_2, CH_4, Hg^0, DMHg) (Andersson et al., 2008; White, 2010). Meanwhile, in incubation experiments the isotope labeled Hg species added may behave differently from those in ambient seawater that are binding to ligands (Lamborg et al., 2004). To provide more reliable estimates on Hg reaction rates (including abiotic methylation), these differences should be addressed in future studies: one possible solution for the first difference is to conduct the incubation experiments *in-situ* the seawater column; for the second limitation, pre-equilibrium should be achieved between ambient and newly added Hg species before starting the incubation experiments.

3. Mercury methylation by anaerobic microbes in anoxic microenvironments

While seawater rarely reaches anoxic conditions across the world's oceans, anoxic microenvironments are known to exist amid oxic seawater. Such anoxic microenvironments include zooplankton guts (Tang et al., 2011), fecal pellets (Alldredge & Cohen, 1987), and marine particles (Bianchi et al., 2018), especially the macroscopic organic-rich marine particles known as marine snow (Shanks & Reeder, 1993). Besides providing anaerobic conditions, the microniches also provide inorganic Hg substrate (Sunderland et al., 2009) and OM that supports activities of heterotrophic microbes (Azam & Long, 2001; Tang et al., 2011). Therefore, such anoxic microenvironments may serve as hotspots for Hg methylation mediated by anaerobic Hg methylators, thus at least partially solving the paradox between oxic conditions in seawater and anoxic conditions required by anaerobic Hg methylation (Figure 4). Because anoxic conditions are resulting from fast oxygen consumption during OM respiration in these microenvironments (Alldredge & Cohen, 1987; Ploug et al., 1997; Tang et al., 2011), enhanced Hg methylation in these microniches would align with the putative association between Hg methylation and OM remineralization. Upon verification, this Hg methylation pathway has an important implication in MMHg bioaccumulation in marine food webs. The MMHg produced within the anoxic microniches can be consumed by zooplankton. This would be a shortcut for MMHg bioaccumulation which otherwise starts from seawater. Especially, the MMHg produced in the guts can be directly taken up by the host zooplankton, thus constituting an unexplored source of MMHg that starts bioaccumulation at a higher trophic level (Gorokhova et al., 2020; Pućko et al., 2014).

The hypothesis of Hg methylation in potentially anoxic particles can be traced back to over 10 years ago (Sunderland et al., 2009), and an increasing number of studies have been conducted to test the hypothesis of Hg methylation in anoxic microenvironments since ∼5 years ago. While it is well established that anaerobic microbes methylate inorganic Hg in anoxic marine sediments (King et al., 1999; Merritt & Amirbahman, 2009), few studies have directly investigated potential Hg methylation in anoxic particles within oxic water column. The first study testing the hypothesis used the seawater incubation approach with addition of isotopically enriched Hg species, in which coastal seawater was incubated with laboratory-generated particles at different size fractions, including marine snow (>300 μm), particles 8–300 μm, and particles 0.2–8 μm (Ortiz et al., 2015). The inorganic $^{200}Hg^{2+}$ spiked was methylated in the potentially anoxic larger particles (> 8 μm) within oxic seawater at the rates comparable to those in sediments. The experiment conducted in a freshwater lake in Western Europe (Lake Geneva) is the only other study examining

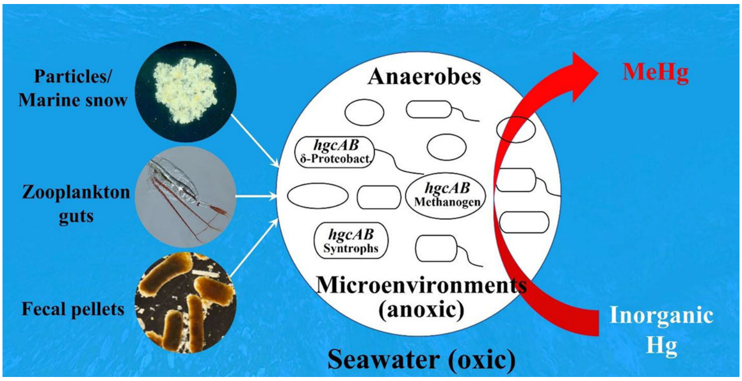

Figure 4. Methylation of Hg by anaerobic microbes carrying *hgcAB* gene cluster in anoxic microenvironments within oxic seawater.

Hg methylation in anoxic particles using addition of isotopically enriched Hg species. Methylation rate constants (k_m) of spiked inorganic $^{199}Hg^{2+}$ in settling particles (1.6×10^{-2}–6.5×10^{-2} d^{-1}) within oxic water column was one order of magnitude higher than those in sediments (1.0×10^{-3}–6.8×10^{-3} d^{-1}), yet the demethylation rate constants (k_d) of spiked ^{201}MMHg were similar in both compartments (0.086–0.219 d^{-1} in particles and 0.064–0.330 d^{-1} in sediments). Therefore, Hg methylation *in-situ* in the particles likely contributed to its ~10-fold higher MMHg concentrations (0.62 ± 0.04–11.38 ± 0.02 ng·g^{-1}) and ratios in Hg_T (0.4%−9.6%) comparing to sediments (MMHg concentration: 0.31 ± 0.03–1.67 ± 0.02 ng·g^{-1}; MMHg ratios in Hg_T: 0.2%−0.8%) (Gascón Díez et al., 2016). The Hg methylation in sinking particles could be associated with activities of sulfate-reducing bacteria (SRB), important Hg methylators in anoxic environments, as suggested by the positive correlation between Hg methylation and sulfate consumption and their concomitant inhibition in the sinking particles amended with molybdate, a special inhibitor for sulfate reducing metabolism. While the two studies conducted laboratory-based experiments to examine the potential Hg methylation in anoxic particles, another research used the Baltic Sea Reference Metagenome dataset to study the distribution of the *hgcAB* gene cluster in the Baltic Sea (Capo et al., 2020). The *hgcAB* genes were found in the metagenome of marine snow from oxic waters, indicating the possible occurrence of anaerobic Hg methylation in anoxic microniches within oxic seawater. However, contradicting to the view that settling particles are Hg methylation hotspots in seawater, sinking particles in the Central Tropical Pacific Ocean were depleted in MMHg relative to phytoplankton biomass (Munson et al., 2015).

Zooplankton gut is another type of anoxic microenvironments that can serve as hot spots for anaerobic Hg methylation, as suggested by recent studies (Gorokhova et al., 2020; Wang, 2019). An examination on the occurrence of *hgcA* gene in the three main clades (*Deltaproteobacteria, Firmicutes and Archaea*) in the gut microbiome of dominant zooplankters in the Northern Baltic Sea, including two cladocerans (*Bosmina coregoni maritima* and *Cercopagis pengoi*) and four copepods (*Acartia bifilosa, Eurytemora affinis, Pseudocalanus acuspes* and *Limnocalanus macrurus*), showed that the *hgcA* gene belonging to *Deltaproteobacteria* and *Firmicutes* was found in the gut microbiome of all copepods but neither cladocerans (Gorokhova et al., 2020). These findings suggest that endogenous Hg methylation may occur in zooplankton guts and contribute to spatial-temporal MMHg variability in the water column and food webs of the Baltic Sea. However, another gene required by Hg methylation (*hgcB*) was not examined in this study and whether the involving microbes methylate Hg in the copepod guts remains unexamined. Wang (2019) also tested the hypothesis, by conducting seawater incubation experiments with addition of inorganic $^{202}Hg^{2+}$ and a key zooplankton species (*Calanus hyporboreus*) in the Arctic Ocean. No enhancement of Hg methylation was observed in the copepod microenvironments (guts and fecal pellets), suggesting that such anoxic microniches are unlikely hotspots for Hg methylation in the Arctic Ocean.

As aforementioned, contradictory results were found in testing the hypotheses of anaerobic microbial Hg methylation in anoxic microniches within oxic waters, thus providing some evidence but not reaching convincing conclusions in verifying this pathway of Hg methylation in oxic seawater. Future research is warranted, especially a combination of incubation experiments determining Hg methylation, occurrence and expression of the *hgcAB* genes, and measurements of MeHg concentrations in the field, to further elucidate the role of this pathway in marine MeHg production. It is not surprising if anaerobic Hg methylation in anoxic microniches were confirmed, given the molecular evidence of SRB found in the ocean's three major oxygen minimum zone (OMZs, with DO $< 20\text{–}45\,\mu\text{mol kg}^{-1}$ (Gilly et al., 2013)) (Canfield et al., 2010; Carolan et al., 2015; Fuchs et al., 2005) likely in anoxic microenvironments like millimeter scale marine snow (Shanks & Reeder, 1993). Modeling study by Bianchi et al. (2018) suggests that sulfate reduction in large marine particles has a contribution of 0.1% of particulate organic carbon (POC) respiration throughout the tropics, coastal regions and the subarctic North Pacific, and up to ∼1% of POC decomposition in OMZs. If Hg methylation were coupled with the sulfate reduction in anoxic particles, the contribution variation may partly explain the large variability in correlations between Hg methylation and OM remineralization observed across the world oceans (Bowman et al., 2020a; Mason et al., 2012). Meanwhile, the heterogeneity of sulfate reduction contribution also suggests that the to-be-verified methylation pathway may have totally different contributions in forming seawater MeHg in different regions and depths. If this pathway proves true in the future, it is important to quantify its contribution in forming MeHg in marine waters from different regions and depths across the world ocean.

4. Mercury methylation by aerobic microbes

Another possible pathway for Hg methylation in oxic seawater is the aerobic microbial Hg methylation, which may proceed in the mechanism associated with *hgcAB* genes or other unidentified metabolic processes (Figure 5) (Podar et al., 2015). For a long time, aerobic microbial Hg methylation has been deemed impossible because all the identified Hg methylators are anaerobes (Bravo & Cosio, 2020; Grégoire & Poulain, 2018). In a study querying *hgcAB* genes in >3500 publicly available microbial metagenomes, seven of the 138 metagenome samples from pelagic marine water column showed the evidence of *hgcAB* (Podar et al., 2015). For the first time, the possibility of Hg methylation by aerobic microorganisms was implied. Soon later, the potential occurrence of aerobic microbial Hg methylation was proposed, as a marine microaerophilic nitrite-oxidizing bacterium (*Nitrospina*) carrying *hgcAB*-like genes was considered a potential Hg methylator in the Antarctic sea ice (Gionfriddo et al., 2016).

The findings of *hgcAB*-like genes in metagenome from marine environments started a wave of studies screening seawater metagenomes and metatranscriptomes for the *hgcAB*-like genes' presence and expression, respectively (Bowman et al., 2020b; Lin et al., 2021; Tada et al., 2020, 2021; Villar et al., 2020). Recently, Villar et al. (2020) analyzed 243 and 187 *Tara* Oceans seawater metagenome and metatranscriptome samples which were collected from 68 and 108 open ocean sites, respectively. These sampling sites covered all ocean basins except the Arctic Ocean. The results showed high abundance of *hgcAB* genes in 77 metagenomes across all oceans studied, corresponding to the taxonomic relatives of known Hg methylating bacteria from *Deltaproteobacteria*, *Firmicutes* and *Chloroflexi*. Being identified as the predominant and widespread microorganism carrying and actively expressing the *hgcA* gene, *Nitrospina* was postulated to be a major Hg methylator in the global oceans. The potential role of *Nitrospina*-like bacteria as Hg methylators in marine waters was also suggested by recent studies surveying Hg_T and MeHg concentrations and *hgcAB* genes in the western North Pacific Ocean (i.e., the East China Sea, the Oyashio region, and the Kuroshio regions) (Tada et al., 2020, 2021). In the metagenomic analyses, the researchers used paired-end reads and assembled contigs for *hgcAB* enumeration

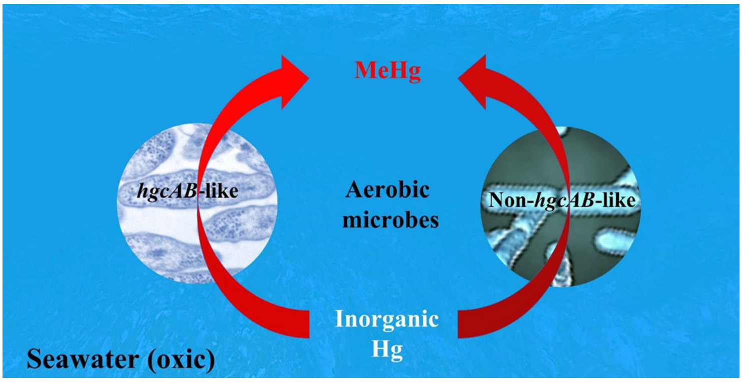

Figure 5. Methylation of Hg by aerobic microbes in oxic seawater.

and phylogenetic analyses in the water column. The results showed that *hgcAB* genes were abundant in the MeHg-rich mesopelagic layers of these regions, and that the *hgcAB* genes detected were likely affiliated with *Nitrospina*-like bacteria. Therefore, *Nitrospina*-like bacteria were presumed to be potential Hg methylator in the mesopelagic zone in the western North Pacific Ocean. Using PCR amplification and shotgun metagenomics, Bowman et al. (2020b) screened for but failed to find the *hgcAB* gene cluster in Arctic Ocean seawater. However, two of the seven stations sampled showed the presence of a paralog of the *hgcA* gene (*cdhD*). While *Nitrospina* known to possess *hgcA*-like genes was detected in the Arctic Ocean, it remains unknown whether the *cdhD* gene observed was affiliated with the bacteria.

These findings reveal the diversity of microbial communities that may possess Hg methylating capabilities and call for more studies on *hgcAB*-like genes and their expressions across different environments including oceans. Given the different methods employed and the difficulties introduced in directly comparing results, it would be useful to establish a more reliable and standardized protocol and an open access library compiling the investigation results (Bravo & Cosio, 2020). It can be expected that a growing number of metagenomic and metatranscriptomic studies would identify more putative Hg methylators carrying and expressing the *hgcAB*-like genes. However, the presence and expression of the *hgcAB*-like genes do not necessarily confer the capability for Hg methylation, which relies on intracellular Hg transport and other unknown biochemical transformations (Podar et al., 2015). For example, Podar et al. (2015) cultured *Pyrococcus furiosus*, the species carrying and expressing a fused hgcAB-like genes, to test its Hg methylating capabilities but did not observe positive results. Therefore, even if more putative aerobic Hg methylators were identified, it is necessary to isolate these species (i.e., *Nitrospina*) and test their Hg methylating capability. To examine the hypotheses of aerobic microbial Hg in oxic seawater, quantitative estimates on their MeHg production in natural marine environments are also required. In addition to the *hgcAB*-like pathway, it is possible that inorganic Hg^{2+} can be methylated by aerobic microbes in oxic seawater through unidentified metabolic mechanism(s) (Bowman et al., 2020b). If the non-*hgcAB*-like biological Hg methylation mechanisms proves true, such metabolism might have more diversity among microorganism communities, just as the *hgcAB*-like-involved Hg methylation do (Podar et al., 2015). However, such mechanisms remain to be identified and investigated by future studies.

5. Concluding remarks

Seawater MeHg is of great importance due to its bioaccumulation to marine animals and human being. Globally, direct atmospheric deposition, riverine transport and sediment production are not considered major sources of MeHg in seawater. Instead, methylation of inorganic Hg *in-situ* in the water column has been regarded the major source of seawater MeHg, which, however, remains puzzling by the known anaerobic Hg methylation requiring anoxic conditions rarely found in marine waters. To explain the Hg methylation in oxic seawater, three Hg methylation pathways have been proposed and investigated in previous studies: (1) Hg methylation by abiotic processes in seawater; (2) anaerobic Hg methylation in anoxic microenvironments within oxic seawater; and (3) Hg methylation by aerobic microbes in oxic seawater. While all three pathways remain to be further verified and studied, at least one of them and maybe all three are probably occurring and jointly contribute to the seawater MeHg in the world oceans.

Abiotic Hg methylation, especially non-photochemical Hg methylation by humic substances and methylcobalamin, could be important sources of seawater MeHg, although photochemical Hg methylation is likely of minor contribution. Their contributions remain unclear largely due to our limited understanding in rates and mechanisms of the chemical reactions of Hg with these methyl donors. Anaerobic Hg methylation in anoxic microenvironments would align with observed association between Hg methylation and OM remineralization, despite no concluding results have been achieved in testing this methylation pathway. The wide presence of a variety of anoxic microenvironments such as zooplankton guts, fecal pellets, and marine particles and the findings of SRB within oxic oceans support this anaerobic Hg methylation in seawater. As MMHg produced in anoxic microniches can be directly consumed by zooplanktons, this pathway implies a possible shortcut for MMHg bioaccumulation. This anoxic microenvironment Hg methylation pathway may exhibit significant spatial heterogeneity across the world oceans, as suggested by the large variability of correlations between Hg methylation and OM remineralization and between sulfate reduction and OM respiration in different sea regions. The recently revealed great diversity of *hgcAB* genes among microorganisms opens the venue for exploring possible aerobic Hg methylation pathways, as exemplified by *hgcAB*-like genes-bearing *Nitrospino* being suggested as a potential Hg methylator whose Hg methylation capability remains to be verified though.

For Hg methylation in seawater, despite some progresses made and summarized in this paper, our understanding is limited and more studies are warranted in the future. Here we discuss some perspectives on future research directions in this area. Development and application of new techniques would greatly facilitate studies on Hg methylation in seawater. For example, new techniques quantifying Hg isotope fractionation shed new lights in tackling the challenge in delineating abiotic methylation from biotic methylation, although more efforts are warranted before its maturing application in studies on seawater Hg methylation. It is also imperative to further improve current methodologies and approaches used in the laboratory to make laboratory studies more environmentally relevant and compatible across different studies. For example, the widely used approach of seawater incubation with isotopically labeled Hg species has deficiencies of unexpected high reaction rates and unexplainable methylation and demethylation immediately after Hg addition (Wang et al., 2020), which are likely caused by differences in incubations from ambient seawater. To provide more reliable results on Hg reactions in seawater, this approach needs to be improved by addressing these differences. For another example, it is useful to establish a standardized protocol and an open access library for *hgcAB* screening research so the results from different studies can be directly compared. Besides methods improvement, integration of different approaches is also of great importance. To reach convincing conclusions regarding the pathway of anaerobic Hg methylation in anoxic particles within oxic seawater, comprehensive studies combining incubation experiments determining Hg methylation, occurrence and expression of the *hgcAB* genes, and measurements of MeHg concentrations in the field will help. Although increasing studies have suggested aerobes (i.e., *Nitrospina*) carrying *hgcAB* genes as potential Hg methylators, studies expanding the screening of such aerobes and examining whether they are capable of methylating inorganic Hg are needed in order to confirm the aerobic Hg methylation pathway. Finally, it should be noted that Hg methylation in seawater is affected by a variety of physical-chemical-biological factors including temperature, redox potential, pH, speciation and concentration of inorganic Hg, DOM and microbial community structure (Ma et al., 2019; Regnell & Watras, 2019). Different pathways of Hg methylation in seawater and their environmental relevance, upon further elucidated, are receiving a combined impact from these factors that often interact with each other. Therefore, we call for more systematic and in-depth investigations on factors impacting different pathways of Hg methylation in seawater. Meanwhile, MeHg in seawater is the net results of methylation, demethylation and transportation (Bravo & Cosio, 2020). Studies of methylation should not be isolated, and systematic studies on these processes will benefit the elucidation of Hg methylation pathways and understanding of MeHg profiles in seawaters.

Acknowledgments

This is contribution number 1375 from the Southeast Environmental Research Center in the Institute of Water & Environment at Florida International University.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

Authors gratefully acknowledge National Science Foundation programs (ECS1905239) for the support of the work.

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