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Shining light on recent advances in microbial mercury cycling

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Abstract

Mercury (Hg) is a global pollutant emitted primarily as gaseous Hg^0 that is deposited in aquatic and terrestrial ecosystems following its oxidation to Hg^{II}. From that point, microbes play a key role in determining Hg's fate in the environment by participating in sequestration, oxidation, reduction, and methylation reactions. A wide diversity of chemotrophic and phototrophic microbes occupying oxic and anoxic habitats are known to participate directly in Hg cycling. Over the last few years, new findings have come to light that have greatly improved our mechanistic understanding of microbe-mediated Hg cycling pathways in the environment. In this review, we summarize recent advances in microbially mediated Hg cycling and take the opportunity to compare the relatively well-studied chemotrophic pathways to poorly understood phototrophic pathways. We present how the use of genomic and analytical tools can be used to understand Hg transformations and the physiological context of recently discovered cometabolic Hg transformations supported in anaerobes and phototrophs. Finally, we propose a conceptual framework that emphasizes the role that phototrophs play in environmental Hg redox cycling and the importance of better characterizing such pathways in the face of the environmental changes currently underway.

Key words: mercury methylation, methylmercury demethylation, biogeochemistry, photosynthesis, mercury redox cycling, climate change

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Introduction

Mercury (Hg) is a global pollutant emitted from natural sources such as volcanic activity and forest fires and anthropogenic sources such as mining and coal combustion (Obrist et al. 2018). Hg is emitted primarily in its elemental and highly volatile form Hg^0, which can travel in the atmosphere for up to a year before being deposited in aquatic and terrestrial ecosystems as oxidized Hg^{II} (Selin et al. 2007). From that point, Hg can be subject to a variety of transformations including burial into sediments; reduction, which results in Hg^0 re-emission to the atmosphere; and methylation, which converts inorganic Hg to toxic monomethylmercury (MeHg) that bioaccumulates in animals (Sunderland 2007) and plants such as rice (Zhang et al. 2010).

Microbes play a key role in Hg transformations. They can produce or degrade MeHg, reduce Hg^{II}, oxidize Hg^0, and sequester a variety of Hg chemical species (as summarized by Barkay and Wagner-Dobler 2005 and Grégoire and Poulain 2014). Generally speaking, microbial Hg transformations occur through cometabolic processes (e.g., encoded by the *hgcAB* gene cluster) or dedicated detoxification strategies (e.g., encoded by the *mer* operon). Hg sequestration can occur through dedicated pathways (e.g., phytochelatins binding Hg (Rauser 1990; Kawakami et al. 2006)) or cometabolic processes (e.g., HgS formation during photosynthesis (Kelly et al. 2007)). Indeed, a wide diversity of

microbes can mediate Hg cycling pathways in a variety of habitats; aerobic, anaerobic, chemotrophic, and phototrophic microbes all influence the fate of Hg in the environment.

In an earlier review, we synthesized the state of knowledge on Hg transformations mediated by phototrophic microbes (Grégoire and Poulain 2014). We highlighted that phototrophic Hg cycling pathways were poorly understood compared with their chemotrophic counterparts. We also discussed why this was an important knowledge gap to address because of the drastic changes predicted to occur in phototrophic communities in response to global environmental changes such as the increased frequency, magnitude, and duration of phytoplankton blooms (Krabbenhoft and Sunderland 2013).

Although the environmental contributions of phototrophs to environmental Hg cycling remain understudied compared with their chemotrophic counterparts, considerable research has been done in recent years to better understand the role of phototrophs in the global Hg cycle. Here, we offer an update to our initial literature review comparing chemotrophic and phototrophic Hg cycling pathways including 68 research papers published since 2014 (Grégoire and Poulain 2014). Our objective with this review was to summarize the recent advances in our understanding of chemotrophic and phototrophic Hg cycling pathways. As part of this, we highlight outstanding knowledge gaps pertaining to microbially mediated Hg cycling emphasizing recent efforts that have helped better understand the role of phototrophs in Hg cycling. Ultimately, we aim to provide recommendations on how to better characterize the environmental and ecological context of microbial Hg cycling in future research.

Chemotrophic mercury transformations

Chemotrophic mercury methylation

Chemotrophic Hg methylation continues to be the most studied microbially mediated Hg transformation, which is unsurprising given the health concerns surrounding MeHg. At the time of our initial review, the discovery of the *hgcAB* gene cluster encoding for Hg methylation had just been published (Parks et al. 2013). Since this transformational finding in the field of Hg research, there has been a surge in the number of studies investigating the physiological and environmental controls of Hg methylation.

On the mechanistic front, computer modeling has shown that the corrinoid protein encoded by *hgcA* initiates a key step in MeHg formation by transferring a negatively charged methyl carbanion to an Hg^{II} substrate (Zhou et al. 2014). This process is thought to occur on the inner side of the cell membrane based on observations in spheroplasts (i.e., bacteria partially/wholly devoid of a cell wall) generated from well-characterized Hg-methylating bacteria (Schaefer et al. 2014b). With respect to the physiology of Hg methylation, gene deletions targeting *hgcAB* in *Geobacter sulfurreducens* PCA, a well-known Hg methylator with proven Hg redox cycling capabilities, resulted in increased Hg uptake, Hg^{II} reduction, and Hg^{0} oxidation (Lin et al. 2014a; Qian et al. 2016). In contrast, deleting the genes encoding for the electron transport machinery essential to Hg^{II} reduction (e.g., encoding for cytochrome c synthesis) in *G. sulfurreducens* increased the abundance of proteins involved in the metabolism of C1 compounds potentially involved in Hg methylation (Qian et al. 2016). These studies suggest that Hg methylation and Hg reduction can compete for common Hg or metabolic substrates inside the cell and support the presence of common physiological controls for both transformations. Further physiological characterization of strains capable of a suite of Hg transformations are required to identify potential the metabolic coupling points that exist for competing Hg transformations.

The discovery of the *hgcAB* gene cluster has revealed a broader diversity of microbes that can potentially methylate Hg compared with what was known four years ago (Podar et al. 2015). Previously, representatives within the sulphate-reducing bacteria (SRB) (Choi et al. 1994a, 1994b), iron-reducing

bacteria (Fleming et al. 2006) and methanogens (Han et al. 2010; Hamelin et al. 2011; Yu et al. 2013) were known to methylate Hg. Homologues for *hgcAB* have now been identified in representatives of the phyla Chloroflexi and Firmicutes (Schaefer et al. 2014a; Christensen et al. 2016); a compilation of microbial strains harbouring the *hgcAB* sequence has been published elsewhere (Paranjape and Hall 2017). Most recently, robust Hg methylation was demonstrated in several cultured methanogen strains (Gilmour et al. 2018). Such studies exemplify how *hgcAB* genes can be used to identify Hg methylators across diverse clades of microbes and provide insight into the environmental controls of Hg methylation that exist in a variety of habitats.

Mining existing (meta)genomic information for *hgcAB* sequences has revealed several new environments that can potentially support Hg methylation including invertebrate digestive tracts, permafrost soil, hypoxic coastal areas, soda lakes, and thermal springs (Podar et al. 2015). In addition, a number of field studies have evaluated the presence or quantified the abundance of *hgcA* gene or *hgcAB* genes in habitats including wetland sediments (Bae et al. 2014; Schaefer et al. 2014a; Graham et al. 2018), wastewater treatment plants (Bravo et al. 2018), rivers near chlor-alkali plants (Bravo et al. 2016), lake sediments (Ma et al. 2017b), river biofilms (Dranguet et al. 2017), hydroelectric dam sediments (Ma et al. 2017a), rice paddies (Su et al. 2016; Vishnivetskaya et al. 2018), and Antarctic sea ice (Gionfriddo et al. 2016). If the number of studies cited above is any indication, the number of habitats that can support Hg methylation will continue to grow, which will help identify novel and potentially overlooked Hg methylation hotspots in the environment.

Several of the above-mentioned studies have assessed the distribution the *hgcAB* gene cluster alongside the abundance of marker genes used as proxies for microbial metabolisms that support Hg methylation. Studies using genes such as the *dsrAB* genes (encoding for subunits of the dissimilatory sulphite reductase (EC 1.8.99.5)) and the *mcrA* gene (encoding the methyl-coenzyme M reductase (EC: 3.1.21)) as proxies for sulphate reduction and methane cycling, respectively, have linked the abundance of Hg methylation genes to different metabolic functional groups (Bae et al. 2014; Gionfriddo et al. 2016; Dranguet et al. 2017; Ma et al. 2017b; Bravo et al. 2018). These studies have led to the discovery that syntrophic microbes, such as those that rely on interspecies hydrogen and acetate transfer following propionate fermentation for growth, play an important role in Hg methylation (Bae et al. 2014; Bravo et al. 2018) in environments depleted in sulphate and iron (e.g., terminal electron acceptors) (Yu et al. 2018). The findings concerning syntrophs highlight the importance of moving away from studies that use single model organisms to better address how complex microbial assemblages can influence MeHg production in the environment.

Despite the surge in studies investigating Hg methylation in microbes, whether a physiological purpose for this Hg transformation exists remains unclear. Hg methylation was once thought to be a detoxification strategy, as studied in the fungus *Neurospora crassa* (Landner 1971). However, experimental evidence in other microbes, including bacteria and archaea, are currently lacking. Much of the evidence published to date supports that Hg methylation is a cometabolic, accidental process. In support of cometabolic Hg methylation, recent studies have shown that organic carbon source composition (Bravo et al. 2016; Christensen et al. 2018), electron acceptor availability (Bravo et al. 2018; Yu et al. 2018), and salinity (Bravo et al. 2016) appear to control the distribution *hgcAB* genes. With some of the genetic determinants for Hg methylation now in hand, the field is ripe to explore the physiological and evolutionary context of Hg methylation in a variety of model organisms.

Despite the recent emphasis on the genetic basis of Hg methylation, research addressing the fundamental aspects of Hg bioavailability to methylators continues to expand. Previously, it was thought that Hg methylation was limited by the availability of inorganic Hg substrates such as HgS, which was considered poorly bioavailable to methylators in sulphidogenic environments (Liu et al. 2009). The importance of HgS as a substrate for methylation has recently been revisited in the context of

how HgS nanoparticle formation controls Hg bioavailability to methylators under anoxic conditions. It has been shown that HgS particles tend to agglomerate, becoming more crystalline and less bioavailable as they age in the presence of dissolved organic matter (DOM), which can decrease Hg methylation (Pham et al. 2014). In contrast, it has also been shown that methylation of HgS can increase in the presence of DOM as a function of thiol content, preventing large and poorly bioavailable HgS aggregates from forming (Graham et al. 2013; Graham et al. 2017). Aside from thiols, it has been suggested that amine and, to a lesser degree, carboxyl functional groups, can also control HgS aggregation once the binding sites of thiols have been saturated at high Hg to DOM ratios (Mazrui et al. 2018). These studies suggest that the controls on HgS nanoparticle formation are complex and reveal the transient nature of how HgS species exert dynamic controls on Hg bioavailability to Hg methylators.

The bioavailability and toxicity of Hg are controlled, in part, by its affinity for thiol-bearing molecules such as cysteine. For the sake of brevity, we have omitted discussing mechanisms for Hg uptake and toxicity in this section as these topics have been recently reviewed elsewhere (Hsu-Kim et al. 2013; Grégoire and Poulain 2014; Parks and Smith 2016; Mahbub et al. 2017). Instead, we briefly focus on recent work addressing the role of DOM and thiol-bearing ligands in mediating Hg bioavailability to Hg methylators.

In a recent study using the model Hg-methylating bacterium *G. sulfurreducens* PCA, cysteine inhibited Hg methylation at low concentrations (0.01 to 0.1 μM) but stimulated Hg methylation at higher concentrations (100 to 1000 μM) when experiments were run for 144 h vs 4 h (Lin et al. 2015). One potential explanation provided for this trend was that thiols mobilized Hg from binding sites on the cell membrane to the cytoplasm, where Hg was more bioavailable for methylation (Liu et al. 2016). The role of functional groups in the cell membrane was recently highlighted in a study comparing Hg methylation in *Desulfovibrio desulfuricans* ND132 and *G. sulfurreducens* in the presence of two sources of DOM (one of aquatic origin with low aromaticity and the other of terrestrial origin with relatively higher aromaticity) (Zhao et al. 2017). In this study, MeHg production by *D. desulfuricans* increased with DOM concentration, whereas MeHg production in *G. sulfurreducens* decreased (Zhao et al. 2017). Another study examining Hg stable isotope fractionation during Hg methylation in *D. desulfuricans* and *G. sulfurreducens* demonstrated that the same strains accessed different intracellular and extracellular pools of Hg during methylation (Janssen et al. 2016). These studies highlight that strain-specific characteristics can have a considerable impact on Hg uptake and subsequent methylation. Although the exact nature of the differences in characteristics has yet to be properly defined, they are clearly important to consider when extending conclusions drawn from a given model Hg methylator to microbial communities in the environment.

Chemotrophic methylmercury demethylation

Compared with Hg methylation, MeHg demethylation has been relatively understudied, although new mechanistic details have emerged for both reductive demethylation (RD) and oxidative demethylation (OD) pathways. Microbes capable of RD harbour the *mer* operon, which is a series of genes encoding dedicated Hg scavenging, transport, and detoxification machinery (Barkay et al. 2003; Parks et al. 2009). The *mer* operon's expression is induced as a function of intracellular Hg concentration and RD is carried out thanks to the presence of *merB*, which encodes an organomercury lyase (e.g., MerB) that cleaves MeHg into inorganic Hg^{II} and CH_4 (Parks et al. 2009). Hg^{II} is subsequently reduced to Hg^0 via the mercuric reductase MerA and CH_4 and Hg^0 can evade the cell (Barkay et al. 2003). In contrast with RD, OD occurs in the absence of dedicated Hg detoxification machinery and is a non-specific cometabolic process tied to C1 compound metabolism that results in the production of Hg^{II} and CO_2 (Oremland et al. 1991; Hsu-Kim et al. 2013).

Recent work on MerB has shown that conserved cysteine and aspartic acid residues are essential for releasing Hg from MerB's active site following the cleaving of the methyl group (Silva and Rodrigues 2015). When a serine residue was present in place of aspartic acid, MerB lost its specificity for MeHg and was also able to bind copper (Cu), although resupplying MerB with Hg successfully removed Cu from the enzyme's active site (Wahba et al. 2016). These findings demonstrate that MeHg can outcompete Cu for the binding site on MerB, but also highlight functional parallels that may exist between RD and Cu homeostasis that merit further investigation.

Despite MeHg formation occurring predominantly in anoxic environments, broad Hg resistance strategies relying on MerB have largely been associated with aerobes. Recent work with the model anaerobe *Geobacter bemidjiensis* Bem suggests that strategies similar to those encoded by the *mer* operon may be present in anaerobes providing them with a means for RD (Lu et al. 2016). *Geobacter bemidjiensis* supported a suite of Hg transformation pathways including Hg methylation, Hg^{II} reduction via a MerA-like mechanism, and Hg^{0} oxidation (Lu et al. 2016). The latter finding is interesting because, to the best of our knowledge, very few complete *mer* operons have been reported for obligate anaerobes. Although these are not the first observations that anaerobes can mediate several Hg transformations, they do provide an interesting basis from which to investigate the physiological controls of competing Hg transformations that may occur simultaneously.

Similar to the work done on Hg methylation, new studies have addressed how thiol-bearing ligands affect RD. In contrast with inorganic Hg, thiol-bearing ligands had little effect on MeHg bioavailability in bacteria capable of RD (*Escherichia coli* and *Pseudomonas stutzeri*) (Ndu et al. 2016). The same study found a considerable difference in MeHg demethylation rates for the two strains despite comparable bioavailability among the different MeHg complexes tested (Ndu et al. 2016). Similar to what was suggested for Hg methylators, the authors attributed the contrasting results to differences in MeHg bioavailability associated with strain specific characteristics (Ndu et al. 2016). Although the authors demonstrated that non-specific binding of MeHg to heat-killed cells rendered a portion of the MeHg unavailable for demethylation, the exact nature of these binding sites was not further discussed (Ndu et al. 2016)

A newly discovered OD pathway in methanotrophs serendipitously provides additional links between Cu metabolism and MeHg demethylation. Methanobactin, a Cu chaperone molecule synthesized by methanotrophs, was essential for OD (Baral et al. 2014; Lu et al. 2017). Recent findings in the model methanotroph *Methylosinus trichosporium* OB3b showed that MeHg demethylation was dependent on the activity of methanol dehydrogenase (Lu et al. 2017), further supporting a link between C1 metabolism and OD (Hsu-Kim et al. 2013). Given that C1 metabolism is also tied to Hg methylation, these results suggest that the availability of C1 compounds in the environment plays an important role in mediating MeHg accumulation. That being said, when considering the role of methanotrophs in OD and its relevance to the environment, one must remember that in most environments where methanotrophs are active, MeHg degradation via OD could be overwhelmed by the large availability of other reduced C1 compounds (e.g., methane). The environmental relevance of this type of OD remains to be determined.

At the environmental scale, a number of studies have measured MeHg demethylation (many of which were summarized by Paranjape and Hall 2017); however, few of these studies explicitly discuss the direct contribution of microbes to demethylation. The fact that many of these systems are net MeHg sources makes it difficult to investigate the mechanisms supporting MeHg destruction beyond the laboratory scale. Further investigations into the mechanisms of biotic MeHg sinks may yield important clues to mitigating MeHg exposure in the environment. To the best of our knowledge, only one recent study has been published that fits this description. In this work, Kronberg et al. 2018 showed that methanogens are important contributors to OD in a wetland ecosystem known to be a

sink for MeHg. Together with previous work on methanogens, this finding frames methane cycling microbes as key players in controlling MeHg levels in the environment.

Chemotrophic mercury reduction

The mercuric reductase MerA encoded by the *mer* operon continues to be one of the best-studied chemotrophic Hg reduction strategies. Recently, it has been shown that sulphur-oxidizing bacteria carrying *merA* were not only able to reduce HgS minerals in aquatic environments, but also use HgS as a sulphur source (Vazquez-Rodriguez et al. 2015). Although it is well established that MerA relies on the use of nicotinamide adenine dinucleotide phosphate (NADPH) as a redox cofactor for Hg^{II} reduction (Barkay et al. 2003), the link between *mer*-mediated reduction and the redox state of the cell is rarely discussed. Recent work with *Thermus thermophilus* HB27 revealed important links between cellular redox balance, Hg sequestration and MerA activity (Norambuena et al. 2018). *Thermus thermophilus* (alongside other representatives of the *Thermus* genus) harboured genes upstream of *merA* in the *mer* operon encoding for the synthesis of low molecular weight thiols that buffered Hg toxicity prior to Hg^{II} reduction (Norambuena et al. 2018). The synthesis of cellular redox buffering compounds proved essential to supporting this Hg detoxification strategy (Norambuena et al. 2018).

Perhaps by further investigating the influence of redox homeostasis on *mer*-mediated reduction we can gain insights into how such Hg detoxification strategies evolved across different redox conditions throughout Earth's history (Barkay et al. 2010). Therein may lay an explanation for the observation of a MerA-like reductase in the obligate anaerobe *G. bemidjiensis* despite such strategies being largely absent in anaerobes (see the previous section). Perhaps such pathways only occur under specific redox conditions in the environment that support anaerobic metabolism optimized for cell growth and Hg detoxification.

Anaerobes such as dissimilatory metal-reducing bacteria continue to be studied with respect to non-*mer*-mediated Hg reduction pathways. As previously mentioned, work with *G. sulfurreducens* has shown that Hg^{II} reduction increased following the deletion of *hgcAB* (Lin et al. 2014a), as did the abundance of cytochrome-c proteins supporting Hg^{II} reduction (Qian et al. 2016), supporting a physiological link for both of these Hg transformations. Recently, it has also been shown that Hg^{II} reduction in *Shewanella oneidensis* MR-1 increased in the presence of natural organic matter (NOM) (Lee et al. 2018). In this instance, the authors indicated that Hg^{II} reduction increased as a function of electron transfer from *S. oneidensis* to NOM, which led to the formation of free radicals that could reduce Hg^{II} (Lee et al. 2018).

Novel non-*mer*-mediated pathways have also recently been discovered in previously untested organisms. Magnetotactic bacteria are now known to reduce Hg^{II} during microaerophilic growth via coupled redox reactions with biogenic magnetite in the membrane of the magnetosome (Liu and Wiatrowski 2018). Our own research has revealed that Hg^{II} reduction is supported in obligate anaerobes from the order Clostridiales. We observed that Hg^{II} reduction was dependent on the ability of cells to produce reduced redox cofactors (possibly ferredoxin) via fermentation when pyruvate was used as a carbon source (Grégoire et al. 2018). Given that *merA* was absent in these strains, our results support that cells reduced Hg because of its electrophilic nature allowing cells to transfer electron from reduced redox cofactors to Hg during fermentative growth (Grégoire et al. 2018). This finding suggests that fermentative Hg reduction may be an important pathway for Hg redox cycling in environments devoid of light and electron acceptors (Grégoire et al. 2018). Given that fermentative microbes occupy a niche similar to that of chemotrophic Hg methylators (Desrochers et al. 2015), such pathways may also influence the accumulation of MeHg. That being said, the contributions of fermenters to Hg^{II} reduction and the potential influence of such pathways on Hg availability to methylators have yet to be investigated.

Chemotrophic mercury oxidation

Hg oxidation still remains one of the most poorly understood chemotrophic Hg transformations, with the first mechanistic details having only just recently been published. Following the seminal work demonstrating Hg^0 oxidation via redox reactions with thiols in the cell membranes of anaerobes (Colombo et al. 2013), additional evidence has emerged supporting the presence of a similar pathway in other obligate and facultative anaerobes (Colombo et al. 2014; Lin et al. 2014b; Lu et al. 2016). It has also been shown that dead cell material bearing intact thiol groups can catalyze Hg^0 oxidation offering a potentially important route for delivering freshly oxidized Hg^{II} to anoxic environments (Colombo et al. 2014). Hg^0 oxidation is thought to be more important in situations where thiol binding site availability is high relative to low extracellular Hg concentration (Lin et al. 2014b). Given the ubiquitous nature of thiols in bacterial membranes (Yu et al. 2014), Hg^0 oxidation by anaerobes is likely widespread in environments such as waterlogged soils (Mazur et al. 2015; Poulin et al. 2016) and anoxic lake sediments (Bouffard and Amyot 2009) where Hg^0 can dominate Hg speciation. When considered alongside the growing evidence for anaerobic Hg^{II} reduction, these findings show that anaerobes are poised to be key players in controlling MeHg production in anoxic systems by catalyzing a dynamic anaerobic redox cycle.

Phototrophic microbial mercury transformations

As outlined in our previous review, there is a growing body of evidence suggesting that oxygenic and anoxygenic phototrophs can participate in Hg transformations in the environment (Grégoire and Poulain 2014). Phototroph-mediated Hg cycling pathways stand to be important in environments where abiotic photochemical Hg transformations are limited (Poulain et al. 2004). Such habitats could include the metalimnion of thermally stratified lakes (Poulain et al. 2004), microbial mats (Dupraz and Visscher 2005; Polerecky et al. 2007), and photic surface sediments (Sloth et al. 1996; Rossi et al. 2012) where phototrophs thrive at low light intensities. Despite the potential for phototrophs to directly influence Hg speciation, considerably fewer studies have addressed phototrophic Hg cycling in recent years compared with the large body of work that exists on chemotrophs. That being said, recent research at the laboratory scale has advanced our mechanistic understanding of Hg uptake, toxicity, and transformation in a variety of phototrophic organisms.

Phototrophic mercury uptake studies

In our initial review, we detailed the existing body of work on the passive and active Hg uptake pathways in phototrophs (Grégoire and Poulain 2014). At that time, all of the information available on Hg uptake in phototrophs was derived from oxygenic phototrophs such as algae, cyanobacteria, and diatoms. Since then, new mechanistic details have emerged on the uptake of Hg in the model green alga *Chlamydomonas reinhardtii* and, for the first time, in anoxygenic phototrophic purple non-sulphur bacteria (PNSB).

Transcriptomic evidence has suggested that *C. reinhardtii* can actively take up inorganic Hg complexes through divalent metal transporters, and organic Hg complexes through amino acid transporters (Beauvais-Fluck et al. 2017), although this was not directly experimentally tested. A similar mechanism was proposed for model PNSB whereby Hg uptake occurred via Ca^{2+} transport channels as an active process (Kis et al. 2017). These findings echo those for chemotrophic anaerobes where active uptake of Hg occurred through Zn^{2+} or Mn^{2+} transporters (Schaefer et al. 2014b; Stenzler et al. 2017). These studies suggest that Hg uptake via divalent cation transporters is supported across diverse microbial metabolisms. Given the high metal requirements associated with phototrophy, Hg uptake via metal transporters is possibly important and may exert a strong influence on downstream Hg transformations.

Whereas the effects of DOM on Hg bioavailability to chemotrophs have been extensively studied, there is little information available for phototrophs (Zhong and Wang 2009). Microbial phototrophy is not limited to autotrophy. Strategies such as mixotrophy where cells can use light for energy and a diverse carbon pool for biosynthesis, could lead to Hg uptake via the shuttling of Hg-DOM complexes into cells (Chiasson-Gould et al. 2014). To the best of our knowledge, the contributions of mixotrophs to Hg uptake in aquatic food webs have only recently been addressed (Cárdenas et al. 2014; Soto Cárdenas et al. 2018). In these studies, the authors showed that mixotrophic ciliates could incorporate Hg through passive diffusion and active uptake linked to bacterivory (Cárdenas et al. 2014; Soto Cárdenas et al. 2018). Despite mixotrophy being widespread in the environment (Raven 2009), the potential implications of mixotrophy on Hg accumulation in aquatic and terrestrial food webs remain largely unexplored.

Phototrophic mercury methylation

The majority of studies addressing the role of phototrophs in controlling MeHg's fate focus on bioaccumulation in food webs, and fewer studies directly address how phototrophic communities affect Hg speciation in the environment. Most of the recent work has been conducted on periphytic communities. These studies face the challenge of distinguishing the direct involvement of phototrophs in Hg methylation from the indirect role that they have (as primary producers) in supplying nutrients to chemotrophic Hg methylators in the periphytic matrix (Lanza et al. 2017; Bouchet et al. 2018). In most cases, MeHg production increased under conditions of higher photosynthetic activity (Gionfriddo et al. 2016; Olsen et al. 2016; Gentes et al. 2017; Lazaro et al. 2018), but recent work emphasized the importance of considering diel periphytic dynamics in MeHg production (Bouchet et al. 2018).

Currently, there is very little support for phototrophs participating directly in Hg methylation. Aside from the initial research cited in our first review (Pongratz and Heumann 1998; Deng et al. 2013), only one new study has emerged investigating the potential for direct methylation in the cyanobacterium *Nostoc paludosum* that showed no MeHg production (Franco et al. 2018).

Microbial strains in the phylum Chloroflexi, which includes representatives of the anoxygenic phototrophic green non-sulphur bacteria, are now known to host the *hgcAB* gene cluster. However, the gene sequences found to date belong to the chemotrophic Dehalococcoidaceae family (Bae et al. 2014; Schaefer et al. 2014a; Podar et al. 2015). With the increasing diversity of habitats being investigated for Hg methylation, perhaps a phototrophic representative harbouring the *hgcAB* gene cluster capable of methylation may soon be uncovered.

Phototrophic methylmercury demethylation

Previously, there was little to no mechanistic data available for direct phototroph-mediated MeHg demethylation (Grégoire and Poulain 2014). Recently, Kritee et al. 2017 used Hg stable isotope fractionation in *Isochrysis galbana* to demonstrate MeHg demethylation in algal cells. In this study, cells preferentially demethylated lighter MeHg isotopes resulting in a pool of isotopically light Hg^{II} (Kritee et al. 2017). In addition, MeHg demethylation resulted in a positive odd-isotope mass-independent signature that was characteristic of the photochemical destruction of MeHg and similar to the Hg isotope signature observed in a variety of marine and freshwater fish (Kritee et al. 2017). This study highlights the power of Hg stable isotope fractionation to track phototroph-mediated Hg transformations at the environmental scale.

Phototrophic mercury reduction

Most of the previous evidence for phototroph-mediated Hg reduction stemmed from observations and experiments performed with oxygenic phototrophs (Grégoire and Poulain 2014). Recent work

on anoxygenic phototrophic PNSB (Grégoire and Poulain 2016) and Heliobacteria (Grégoire et al. 2018) has provided some of the first mechanistic details for anaerobic phototrophic Hg reduction.

Our work with PNSB demonstrated that Hg^{II} was preferentially reduced during photoheterotrophic growth on reduced organic carbon substrate (e.g., using light as an energy source and generating biomass using an organic carbon source) (Grégoire and Poulain 2016). Under controlled laboratory conditions, we showed that PNSB derived an advantage from sublethal Hg exposure, which we attributed to the ability of Hg to act as an electron sink during phototrophic growth (Grégoire and Poulain 2016). Large peaks of Hg^0 have been reported in the metalimnion of lakes (Poulain et al. 2004), and anoxygenic phototrophs such as PNSB thrive in environments such as the thermoclines and chemoclines of stratified aquatic ecosystems (Schütte et al. 2016) and microbial mats (Schneider et al. 2013). These metabolically versatile microbes stand to be important players in Hg redox cycling in environments where light is attenuated and reduced organic carbon is available. Such habitats are often located at redox interfaces that act as gateways to Hg methylation sites.

Following up on our work with anoxygenic phototrophs, we further discovered that Heliobacteria, a family of spore-forming fermentative photoheterotrophs of the order Clostridiales, were among the most efficient Hg reducers reported to date (Grégoire et al. 2018). No apparent dedicated Hg reduction machinery (i.e., *mer* operon determinants) was found in the genome of *Heliobacterium modesticaldum* Ice1, and Hg^{II} reduction most likely occurred as a cometabolic process related to the availability of reduced redox cofactors (e.g., ferredoxin) (Grégoire et al. 2018). The fact that cometabolic Hg reduction was observed in two phylogenetically and ecologically distinct groups of anoxygenic phototrophs suggest that such pathways may be widespread in anoxic habitats offering phototrophs a means of detoxifying Hg without dedicated enzymatic machinery.

The use of stable Hg isotopes has recently provided unique insights into oxygenic phototrophic Hg reduction. In the same study addressing MeHg demethylation in *I. galbana*, cells reduced lighter Hg^{II} isotopes with the strongest fractionation signature occurring within the intracellular pool of Hg^{II} (Kritee et al. 2017). The authors also observed mass-independent fractionation signatures suggesting that Hg was reduced by free radicals inside the cell following binding to thiol functional groups (Zheng and Hintelmann 2010; Kritee et al. 2017). The prevalence of free radical formation during oxygenic photosynthesis is such that algal cells could be seen as small photoreactors hosting Hg photoreduction. Indeed, this study represents a fascinating case of intracellular metal photoreduction that blurs the lines between abiotic and biotic transformations.

The presence of putative *merA* homologues in the genomes of some anoxygenic phototrophs (Mukkata et al. 2015; Pérez et al. 2018) highlights an interesting question regarding Hg tolerance in phototrophs: do cells preferentially detoxify Hg via cometabolic processes or through the use of dedicated reductases? Currently, it seems that phototrophic Hg reduction occurs mostly as a cometabolic process that relies on core metabolic machinery rather than *mer*-like determinants, which are largely absent in phototrophs. That being said, very few studies have been published on the subject and the presence of such pathways has only been identified for a small number of model organisms. By exploring this question further we will better define the physiological mechanisms supporting phototrophic Hg metabolism. The increasing availability of microbial genomes and genetic tractability of anoxygenic phototrophs should help address this question in future research.

Clearly, phototrophs are more than just an entry point for Hg into food webs. The mechanistic findings mentioned in this section frame photosynthetic redox homeostasis as a metabolic process coupled with Hg reduction. These mechanistic studies further demonstrate that phototrophs can directly impact the substrate of Hg available to methylators via Hg redox cycling. How such interactions play out in the environment remains elusive, however.

Phototrophic mercury oxidation

At present, there is a lack of studies addressing Hg^0 oxidation in phototrophs. This could be related to the challenges associated with working with volatile Hg^0 as a substrate. We speculate that anoxygenic phototrophic bacteria could potentially oxidize Hg^0 through thiol-related mechanisms similar to those outlined in chemotrophic anaerobes based on the fact that Hg is known to bind to thiols in the photosynthetic reaction center of PNSB (Asztalos et al. 2012; Sipka et al. 2017). Currently, the presence of such pathways has yet to be investigated and Hg^0 oxidation in phototrophs has yet to be demonstrated.

Mercury toxicity to phototrophs

Phototrophs appear to mitigate Hg toxicity either via intracellular sequestration or elimination from the cell (e.g., via efflux or evasion). Sequestration strategies come in the form of dedicated chelating molecules such as phytochelatins and metallothioneins (Rauser 1990; Kawakami et al. 2006) and the production of HgS (Kelly et al. 2007), all of which prevent Hg from binding to sensitive target sites inside the cell.

Inside the cell, Hg can interact with a number of proteins that are essential for supporting photosynthetic metabolism. Hg's toxicity is attributable to Hg's affinity for thiol bonds (Rooney 2007) and its ability to substitute for cations that serve as cofactors in enzymatic reactions essential to capturing light energy (Matson et al. 1972; Singh et al. 2012; Zhang et al. 2013). By disrupting protein function, Hg can inhibit electron transport and the ability of cells to generate ATP thereby inhibiting cell growth (Murthy and Mohanty 1993; Kukarskikh et al. 2003; Antal et al. 2009). Although toxicological studies continue to emerge evaluating the ranges of Hg concentrations tolerated by different model phototrophs (Chen et al. 2014; Zhu et al. 2015; Nowicka et al. 2016; Mu et al. 2017), very few offer new mechanistic insights (Grégoire and Poulain 2014).

The recent transcriptomic work with *C. reinhardtii* has provided insights into the genetic response of green algae to Hg toxicity (Beauvais-Fluck et al. 2016; Beauvais-Fluck et al. 2017). Hg exposure led to the disruption of genes involved in motility, cell division, energy metabolism, amino acid production, lipid oxidation, metal transport, and antioxidant enzyme synthesis (Beauvais-Fluck et al. 2017). Although the apparent negative effects on gene regulation did not always manifest as a physiological response (Beauvais-Fluck et al. 2016; Beauvais-Fluck et al. 2017), the authors saw increased photosynthetic efficiency when small levels of MeHg were present (Beauvais-Fluck et al. 2016). These results suggested a possible hormetic effect derived from MeHg exposure that merits further investigation. Based on our own observations in PNSB, there is precedence for sublethal exposure to Hg providing a physiological advantage during phototrophic growth by acting as an electron sink (Grégoire and Poulain 2016). Whether such a pathway is supported in oxygenic phototrophs has yet to be tested and the importance of beneficial or hormetic responses to Hg in the environment remains to be evaluated.

At the time of publishing our 2014 review paper, very little mechanistic information was available on Hg toxicity in anoxygenic phototrophs. This has changed in recent years. Work with PNSB showed that large amounts of Hg^{II} can bind to the photosynthetic reaction center (PS-RC) (Asztalos et al. 2012) and that the vast majority of Hg supplied to PNSB was bound to weak binding sites, rather than to high affinity thiol-bearing sites (Sipka et al. 2017). Although the exact chemical natures of the weak binding sites were not further discussed, one can speculate that these binding sites may have been carboxyl groups that have a lower affinity for Hg (Gu et al. 2011; Mishra et al. 2011; Jiang et al. 2015) and are known to be present in the PS-RC (Knox et al. 2018). Sipka et al. 2017 also demonstrated that Hg toxicity was attributable to a small number of strong thiol-bearing Hg binding sites that disrupted cyclical phosphorylation by inhibiting inter-quinone electron transfer and proton

translocation. Despite the sensitivity of electron transport machinery to Hg, model PNSB strains could tolerate μM levels of Hg before damage to photosynthetic membranes became apparent (Kis et al. 2015).

These new findings illustrate that Hg targets may be similar between oxygenic anoxygenic phototrophs, which is unsurprising given the evolutionary parallels between some components of their photosynthetic machinery. Although the availability of genomic information frame PNSB as excellent models to study Hg toxicity in anoxygenic phototrophs, the response of other clades to Hg has yet to be characterized. For instance, we know very little about Hg interactions with green (non)-sulphur bacteria, aerobic anoxygenic photosynthetic bacteria, Heliobacteria, or purple sulphur bacteria. This information would be useful in revealing the evolutionary and physiological context shaping the response to Hg toxicity among phylogenetically distinct clades of phototrophs. Indeed, the absence of dedicated Hg resistance strategies such as the *mer* operon among anaerobes and phototrophs is puzzling. There appears to be a tight coupling between the presence of oxygen and the evolution of the *mer* operon (Barkay et al. 2010). Anaerobic and anoxygenic phototrophic metabolisms predate the rise of oxygen on Earth and cometabolic processes such as sequestration or the use of excess reducing power to catalyze Hg reduction may have been sufficient to cope with Hg toxicity in the absence of oxygen.

Concluding remarks

Over the last four years, we have observed a shift in the field of research addressing microbial Hg transformations. Investigations into chemotrophic Hg methylation still dominate the literature thanks largely to the discovery of the *hgcAB* gene cluster. With powerful molecular tools in hand, one important frontier in our field is to identify the native function of this gene cluster and the possible role(s) associated with Hg methylation. In addition to gaining fundamental insights into the process, such mechanistic insights may reveal strategies that could help manage Hg pollution.

Important mechanistic details of anaerobic and phototrophic Hg cycling have also emerged, leading us to reconsider the environmental contributions of anaerobic Hg redox cycling pathways. One such contribution is summarized in **Fig. 1**, highlighting a possible role of phototrophs in catalyzing Hg reduction at redox interfaces within a stratified lake ecosystem.

Once deposited into aquatic ecosystems, aqueous Hg speciation is altered such that ageing of Hg complexes occurs, typically leading to low Hg bioavailability over time (**Fig. 1A**-(**1**)). Redox processes catalyzing the transformation of Hg complexes control the delivery of bioavailable Hg to anoxic zones. This occurs by resetting Hg speciation, i.e., remobilizing Hg initially present as poorly bioavailable complexes (e.g., Hg-DOM or Hg-particles) to more mobile and bioavailable species (e.g., Hg^0, **Fig. 1A**-(**2**) and **1B**). This can occur by anaerobic or photobiological redox processes targeting Hg and described in this review, or via heterotrophic or photochemical degradation of the organic ligands to which Hg is bound. Given the increasing importance of anaerobes in Hg^0 oxidation and anoxygenic phototrophs in Hg^{II} reduction, these groups can provide a fresh supply of bioavailable Hg to sites conducive to Hg methylation (**Fig. 1A**-(**3**) and **1B**).

This conceptual redox wheel (Chiasson-Gould et al. 2014) is meant to highlight the potential for highly dynamic yet cryptic Hg redox cycling (**Fig. 1B**). We use the word cryptic here to highlight the fact that no net Hg^0 accumulation may be observed but its production and rapid oxidation may represent an essential step in controlling Hg mobility at, and across, redox interfaces. Furthermore, this conceptual framework illustrates how phototrophs (or other anaerobes) can participate in Hg transformation well beyond their role as MeHg accumulators at the base of food webs. Note that such processes can occur in any stratified environment, whether it is within the metalimnion of lakes, microbial mats, or periphytic communities (**Fig. 1**).

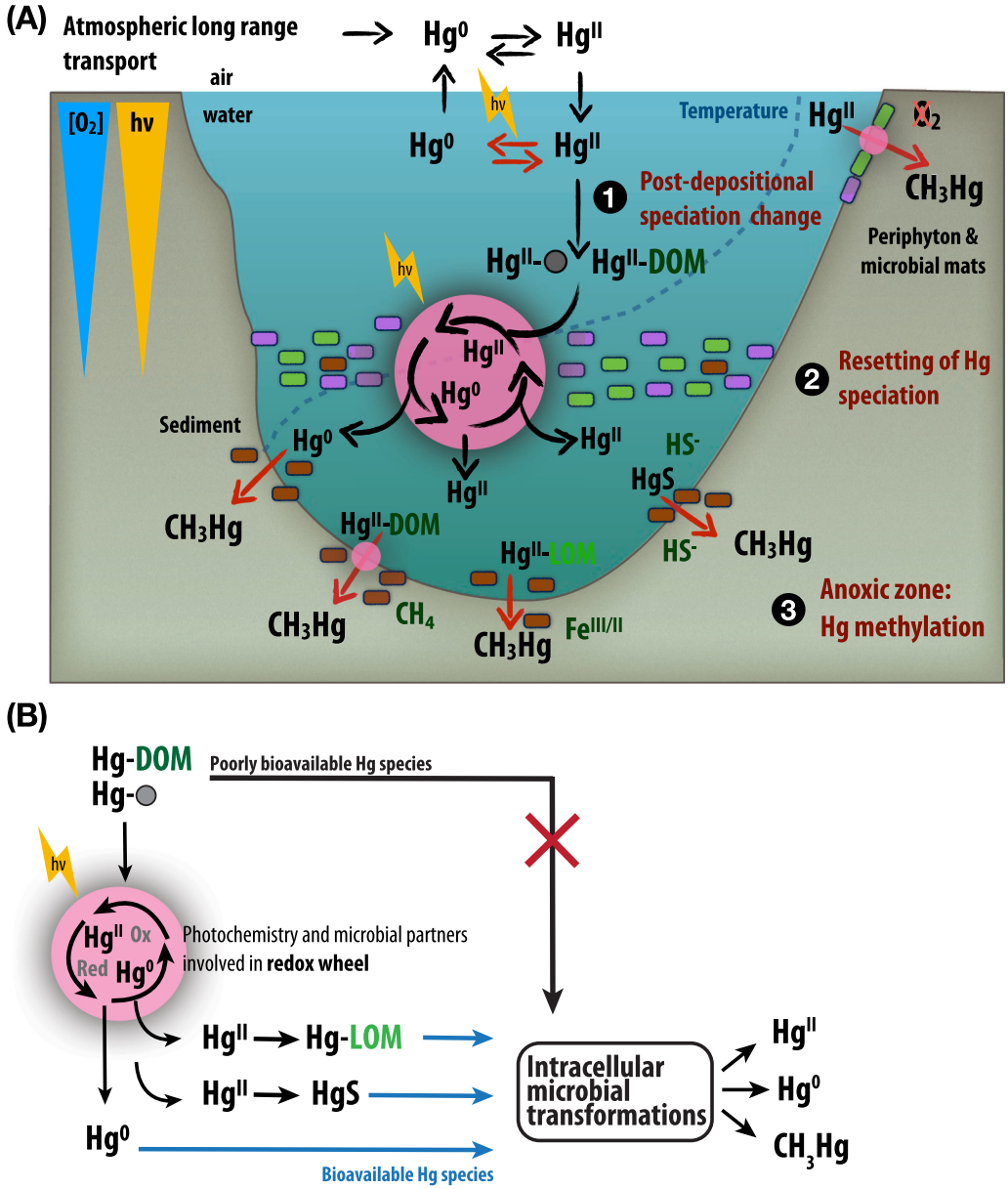

Fig. 1. Conceptual summary for the possible role of phototrophic and anaerobic microbes in controlling Hg bioavailability. Numbers refer to descriptions made in the Concluding Remarks section of the text. The pink disks highlight sites where Hg speciation can be reset via redox processes that directly affect Hg (see text) or the ligands to which Hg is bound (e.g., via heterotrophy or DOM photo-transformation). These processes can occur in oxic or anoxic conditions and be catalyzed by light, microbes, or both. At the ecosystem scale (panel A), anoxygenic phototrophs are represented in green and purple, Hg methylators are represented in brown, dissolved organic matter has been abbreviated as DOM, labile organic matter available to microbes is abbreviated as LOM, and particulate matter is denoted by small grey circles. Hg-DOM represents poorly bioavailable Hg complexes formed with organic matter ligands of a large size. Hg-LOM represents highly bioavailable Hg complexes formed with labile organic matter ligands; these labile organic matter ligands can act as shuttles for Hg inside the cell. Lightning bolts represent light energy (hν) required for photobiological or photochemical processes. Inverted blue and yellow triangles represent oxygen and light energy gradients, respectively. HS^- (sulfide), CH_4 (methane), and $Fe^{II/III}$ (iron oxides) are meant to represent some of the anaerobic metabolisms known to be involved in Hg metabolism: sulphatoreduction, methanogenesis, and ferroreduction, respectively. Panel B was adapted from Chiasson-Gould et al. 2014 and represents the redox wheel in the context of the diversity of Hg species available for microbial transformations.

Although lab studies have afforded the controlled conditions necessary to elucidate new mechanisms for phototrophic Hg transformations, these pathways continue to be understudied in the environment. This knowledge gap will become increasingly important to address in the face of predicted environmental change. Increases in temperature, prolonged ice-free seasons and more intense water column stratification will have a dramatic impact on phototroph dynamics that, in turn, exert important controls on environmental chemistry and metal speciation. Indeed, there stand to be far-reaching impacts on global Hg cycling stemming from changes in phototrophic communities that occupy broad niches in oxic and anoxic habitats.

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Author contributions

DSG and AJP conceived and designed the study. DSG and AJP performed the experiments/collected the data. DSG and AJP analyzed and interpreted the data. DSG and AJP contributed resources. DSG and AJP drafted or revised the manuscript.

Competing interests

AJP is currently serving as a Subject Editor for FACETS, but was not involved in review or editorial decisions regarding this manuscript.

Data availability statement

All relevant data are within the paper.

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