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### Role of phytoplankton in aquatic mercury speciation and transformations

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## **Environmental Context**

Understanding mercury transformations in the aquatic environment is of utmost importance for the improvement of mercury biogeochemical modelling and sound environmental risk assessment. In such a context we discuss critically the advancement in the knowledge on the role of the phytoplankton (algae and cyanobacteria) in mercury cycling and transformations in the aquatic environment. Important research advances revealed that different microalgal species and cyanobacteria contribute to biotic reduction of inorganic mercury to elemental mercury, as well as methylmercury demethylation and transformation of inorganic mercury into metacinnabar, as well as produce different biomolecules which can contribute to abiotic mercury reduction.



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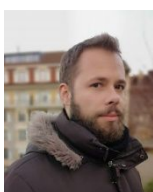
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Thibaut Cossart is a Ph.D. student in Environmental Science at the University of Geneva, Switzerland. He got a Master's Degree in Marine Biodiversity and Biomolecules from the University of Toulon (France). His research is focused on the interactions between phytoplankton and mercury. He highlighted the role of phytoplankton in the biogeochemical cycle of mercury by (i) evaluating the biotic transformations performed by a cyanobacterium and natural phytoplankton communities, (ii) and by determining the effects of thiol-containing bioligands on the bioaccumulation of Hg species by cyanobacteria.



Javier García Calleja He currently is a Ph.D. student in the Amouroux lab at the IPREM, CNRS- UPPA, Pau, France. He holds a BSc in Chemistry and a MSc in Analytical and Bioanalytical Chemistry from the University of Oviedo. His research includes (i) development of mathematical approaches based on isotope pattern deconvolution for studying Hg compound reactivity in *in situ* Hg incubation experiments and (ii) characterization of major bioligands involved in Hg speciation in phytoplankton applying hyphenated techniques based on elemental and mass spectrometry.



João P. Santos holds a BSc in Biology and a MSc in Ecology, Environment and Landscape, and a MSc in Marine Sciences from the University of Porto, Portugal. He worked with the nitrogen cycle communities until he started his Ph.D. Currently, he is a Ph.D student in the Slaveykova's lab at the University of Geneva, where he studies the interaction of diatoms and natural phytoplankton communities with different mercury species, and explore their capability to accumulate, transform and detoxify mercury.



Dr. Elaheh Lotfi Kalahroodi is a postdoctoral researcher in Environmental Geochemistry at the Umeå University in Sweden. Her research is focused on the biogeochemical mechanisms of organic and inorganic contaminants in the environment through isotope fractionation of stable non-traditional isotopes. She studies the controlling factors as the physicochemical conditions on contaminant reactivities. She aims to evaluate and optimize a methodology to trace and quantify the spread of Hg from contaminated sediment sites to surrounding sediment and pelagic and benthic biota using Hg stable isotope measurements.



Dr. Isabelle A.M. Worms is a senior scientist of environmental biogeochemistry and ecotoxicology at the University of Geneva. She is a biochemist with a Master's Degree in molecular chemistry. Since her Ph.D., her research interests include (i) gaining a better understanding of the bioavailability of trace metals; (ii) the development of AF4-ICP-MS to assess the role of natural organic matter on the binding and dispersion of trace metals in surface water; and (iii) identifying key processes (environmental-corona formation, dissolution/formation, and aggregation) involved in nanoparticle stability using quantitative approaches.



Dr. David Amouroux is a Research Director at the French CNRS appointed at IPREM Institute (CNRS-UPPA) and he is responsible of the Research Unit for Environmental Chemistry and Microbiology. He is an environmental and analytical chemist, specifically interested in the cycling and reactivity of contaminants in the environment. Some of his research lines include: (i) transformations and transfer of mercury; selenium and other metal(loid)s at aquatic environments interfaces and (ii) development of analytical and experimental methods using stable isotopes of trace elements to investigate biogeochemical mechanisms in the environment.



Dr. Vera I. Slaveykova is a full professor of environmental biogeochemistry and ecotoxicology at University of Geneva and president of the School of Earth and Environment Sciences. She works on the development of concepts and tools for a better understanding of the fundamental processes governing the behavior of trace elements and nanoparticles, and their interactions with various biotic and abiotic constituents of aquatic systems. Her current research interests and portfolio include (i) speciation and bioavailability of trace elements, mercury, and nanoparticles in the aquatic environment; (ii) aquatic toxicology of inorganic contaminants and nanoparticles; transcriptomics and metabolomics; (iii) community ecotoxicology and biodiversity in aquatic systems.

**27 Abstract**

28 Phytoplankton may directly influence biogeochemical cycling and transformations of mercury  
29 (Hg) through biotic transformations of the accumulated metal via methylation/demethylation and  
30 reduction/oxidation, and indirectly, through the excretion of low and high molecular mass ligands,  
31 likely triggering or influencing different abiotic transformation pathways as well as the  
32 transformations carried by bacteria. However, unlike the extensive work already done on the role  
33 of bacteria in Hg transformations, the current knowledge about the influence of phytoplankton  
34 (algae and cyanobacteria) on such processes is still limited.

35 Critical evaluation of the existing advances in the research topic revealed that different microalgal  
36 species and cyanobacteria contribute to biotic reduction of inorganic mercury (iHg) into Hg<sup>0</sup>,  
37 monomethylmercury (MeHg) demethylation, and transformation of iHg into metacinnabar. The  
38 low and high molecular mass biomolecules released by phytoplankton can complex Hg species  
39 and contribute to abiotic mercury reduction. Despite these advances, the underlying mechanisms  
40 and their importance in the aquatic environment are to be explored and confirmed. The  
41 development of the novel molecular, stable isotope-based, and multi-omics approaches would  
42 provide the further impetus for the understanding of the key interactions between Hg species and  
43 phytoplankton. Such understanding will be of utmost importance for the improvement of the Hg  
44 biogeochemical modelling, mitigation strategies, and rational environmental risk assessment in  
45 changing aquatic environment.

46

47

48 **Keywords:** Mercury cycling, methylmercury, speciation, methylation, demethylation, reduction,  
49 oxidation, algae, cyanobacteria

50

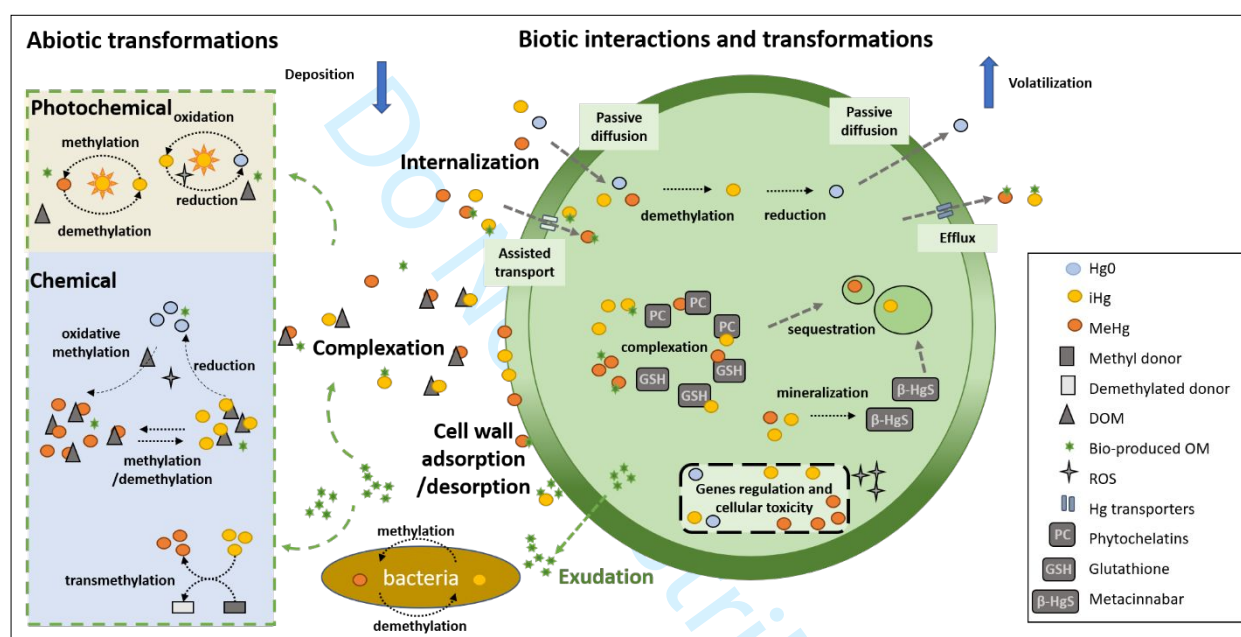
## 51 1. Introduction

52 Mercury is naturally present in the environment, however, since the industrial revolution,  
53 anthropogenic activities have increased the global Hg emissions by a factor of 2-15 and disturbed  
54 Hg biogeochemical cycle (Ariya et al., 2015; Asaduzzaman et al., 2019; Branfireun et al., 2020;  
55 Driscoll et al., 2013), leading to a significant increase in the concentration of various Hg  
56 compounds in the aquatic environment. Once entered into the aquatic environment, Hg  
57 compounds interact with different biotic and abiotic components and undergo numerous  
58 transformations. The major transformation pathways involve the reduction/oxidation of inorganic  
59 mercury (iHg)/elemental mercury ( $\text{Hg}^0$ ) and the methylation/demethylation of  
60 iHg/monomethylmercury (MeHg,  $\text{CH}_3\text{Hg}$ ). iHg and MeHg can accumulate in the aquatic  
61 organisms and MeHg biomagnifies along the food webs, presenting a hazard to higher consumers,  
62 including humans (Sheehan et al., 2014; Yang et al., 2020). The bioconcentration of Hg by  
63 phytoplankton represents one of the main entry steps of Hg into the food web (Dranguet et al.,  
64 2014; Le Faucheur et al., 2014; Wu et al., 2019). The knowledge of various transformation  
65 processes determined by photochemical, chemical, and biologically mediated reactions (such as  
66 the ones performed by phytoplankton) is also crucial for understanding the global  $\text{Hg}^0$  fluxes  
67 (Jiskra et al., 2021).

68 Exploring mercury transformations in aquatic environment is an active research area. Extensive  
69 studies have been already done on the role of bacteria in Hg transformations, as comprehensively  
70 reviewed (Hsu-Kim et al., 2013). Several recent reviews deal with specific transformation  
71 mechanisms and influencing factors, including advances in the knowledge regarding the  
72 methylation (Gallorini and Loizeau, 2021; Paranjape and Hall, 2017; Wang et al.), demethylation  
73 (Barkay and Gu, 2021), production/degradation of MeHg in the cryosphere (Ghimire et al., 2019),  
74 biotic and abiotic degradation of MeHg (Du et al., 2019) and photochemical transformation of Hg  
75 species (Luo et al., 2020). The role of phytoplankton (cyanobacteria and algae) in Hg cycling (i.  
76 e., alteration of Hg redox state, Hg scavenging, potential for methylation), as well as the



77 description of the cellular and molecular targets involved in the toxicity of Hg in phototrophs,  
 78 were thoroughly discussed (Beauvais-Flück et al., 2018; Grégoire and Poulain, 2014). Hg  
 79 bioavailability to phytoplankton (Dranguet et al., 2014; Le Faucheur et al., 2014) and its effects  
 80 to primary producers were also reviewed. In this context, the importance of phytoplankton in  
 81 aquatic mercury transformations was always questioned but never systematically addressed.  
 82



83  
 84 **Figure 1.** Conceptual view of main processes involved in aquatic Hg transformations by  
 85 phytoplankton.  
 86

87 In the present review paper, we focussed on the controls exerted by phytoplankton on the key  
 88 transformations of mercury in the aquatic environment (Fig. 1), in particular their role in the  
 89 complexation, abiotic and biotic transformations of Hg species.

## 90 2. Mercury speciation in aquatic environment

91 In natural waters, mercury is commonly found as iHg, MeHg and Hg<sup>0</sup> with their relative  
 92 abundances being controlled by chemical, physical and biological processes (Brian et al., 2020).  
 93 At environmental conditions, it will be rare to find mercury compounds as a free ion ( $< 10^{-26}$  mol  
 94 L<sup>-1</sup>) (Le Faucheur et al., 2014) but rather forming complexes having different biological reactivity

95 (Ravichandran, 2004). In aquatic environments mercury species are found to be complexed by the  
96 dissolved organic matter (DOM) (Jiang et al., 2017; Klapstein and O'Driscoll, 2018; Lavoie et al.,  
97 2019; Liem-Nguyen et al., 2017; Poulin et al., 2019; Ravichandran, 2004; Wang et al., 2015)  
98 without distinction of the origin or the molecular weight of the organic matter (Chen et al., 2013;  
99 Jiskra et al., 2017; Wang et al., 2022). Among all chemical functional groups present in DOM,  
100 mercury bounds to the hydrophobic and hydrophilic acids including the  $-SH$ ,  $-NH_2$ ,  $-COOH$ ,  $-$   
101  $OH$  (Ravichandran, 2004). The speciation is dependent on the medium composition and will  
102 affect the bioavailability and thus the interactions of mercury species with phytoplankton  
103 organisms (Le Faucheur et al., 2014; Luo et al., 2020).

104

### 105 3. Effect of biomolecules excreted by phytoplankton on Hg speciation

106 Phytoplankton produces various small molecules, including fatty acids, carboxylic acids, amino  
107 acids, and extracellular polymeric substances (EPS, such as polysaccharides, nucleic acid, and  
108 proteins) (Seymour et al., 2017). EPS represents up to 25% of natural organic matter in  
109 freshwaters, especially during algal blooms (Shou et al., 2018; Wilkinson et al., 1997). The EPS  
110 components comprise diverse anionic groups (e.g.,  $-SH$ ,  $-NH_2$ ,  $-COOH$ ,  $-PO_4^{3-}$ ), thus providing  
111 metal-binding properties (Babiak and Krzemińska, 2021). Phytoplankton is also known to release  
112 small thiols with strong capacities to bind metals in their ambient environment (Liu et al., 2020),  
113 which are expected to affect the speciation and thus Hg abiotic and biotic transformations. The  
114 nature and concentration of such small biomolecules vary with the algal species and  
115 environmental factors (Mangal et al., 2019a). For example, the diatom *Phaeodactylum*  
116 *tricornutum* has been reported to release cysteine-like exudates, whereas the coccolithophore  
117 *Emiliana huxleyi* excreted both glutathione- and cysteine-like compounds (Vasconcelos et al.,  
118 2002). The effects of biomolecules released by algae on Hg speciation have been examined in the  
119 field, where dissolved organic carbon and algal exudates are the predominant ligands of Hg in the  
120 rivers and lakes of Long Island Sound (USA)(Lamborg et al., 2004). Six thiols (mercaptoacetic

121 acid, cysteine, homocysteine, N-acetyl-cysteine, mercaptoethane-sulfonate, and glutathione) were  
122 detected with total concentrations of 7-153 nM in boreal lake waters (Bouchet and Björn, 2014;  
123 Liem-Nguyen et al., 2015). Recent studies have shown that several green algae excrete some  
124 ligands, particularly thiol-containing ligands that form strong complexes with Hg species and thus  
125 modify Hg speciation and bioavailability.

126 The interaction of Hg species with EPS is poorly documented although recognized to have a  
127 unique molecular character (Ly et al., 2017; Mangal et al., 2016). EPS were shown to play a  
128 significant role in phytoplankton protection against metal stress (Naveed et al., 2019), suggesting  
129 that the EPS complexes metals, including Hg. For example, EPS protected cyanobacteria from Hg  
130 uptake (Chen et al., 2014). Hg was shown to bind to protein-like material produced by  
131 *Chlorocochus* (molecular weight, MW > 3.5kDa) (Song et al., 2014), and EPS from activated  
132 sludge (MW > 3.5kDa) was shown to bind Hg presumably by electrostatic interactions (Zhang et  
133 al., 2013). Biomolecules released by several microalgae with apparent molecular mass > 1kDa,  
134 likely prevented the induction of Hg microbial biosensor, whereas the presence of smaller  
135 biomolecules (MW 0.3kDa-1kDa) allowed the induction of Hg controlled fluorescence (Mangal  
136 et al., 2019a). Nevertheless, further studies are necessary to explore the relative importance of the  
137 biomolecules released by the phytoplankton species, including thiols and EPS, in Hg speciation  
138 and their role in its transformations in aquatic environments.

139

#### 140 **4. Extracellular transformation pathways of mercury triggered by phytoplankton**

141 In oxic waters, Hg species can be subjected to a series of abiotic transformations, such as  
142 methylation/demethylation and reduction/oxidation, as influenced or not by incident light. The  
143 extent of these transformations depends on the environmental factors and biological activity of  
144 aquatic living microorganisms (Grégoire and Poulain, 2014; Hsu-Kim et al., 2013).

145

##### 146 **4.1. Abiotic reduction**

147 Photochemical reactions are responsible for the reduction of iHg to Hg<sup>0</sup> and Hg<sup>0</sup> oxidation to iHg  
148 (Vost et al., 2012). The extent of these reactions depends on the intensity of ultraviolet radiation  
149 (Black et al., 2012) and the ambient water composition (Lalonde et al., 2001; Whalin et al., 2007).  
150 Although the importance of each reaction is not resolved yet, it is recognized that their kinetics is  
151 strongly affected by Hg speciation, which in turn is modulated by the nature and concentrations  
152 of ligands present in surface waters (Tai et al., 2014; Zhang and Hsu-Kim, 2010). Biogenic DOM  
153 produced by the marine diatom *Chaetoceros* sp. was involved in the photoreduction of iHg  
154 (Lanzillotta et al., 2004). A recent review highlighted that the photooxidation of Hg<sup>0</sup> is mainly  
155 mediated by reactive oxygen species (ROS) (Luo et al., 2020). The ROS generation can also occur  
156 by the absorption of Ultraviolet-B radiation by humic and fulvic-like DOM resulting in various  
157 photochemical transformations involving oxygen. On the other hand, the Hg redox cycle in oxic  
158 surface waters is mainly dominated by the photochemical Hg (II) reduction (Amyot et al., 1997).  
159 Indeed high production of dissolved gaseous mercury (DGM) was correlated to the high  
160 concentration of DOM, in particular thiols binding sites (Ariya et al., 2015).

161

#### 162 **4.2. Abiotic methylation/demethylation**

163 Abiotic methylation can occur through transmethylation with organometallic species (methylated  
164 Pb, I, etc.) and methyl donors such as methylcobalamin, but these pathways are not considered  
165 predominant compared to biotic methylation (Celo et al., 2006; Weber, 1993). Physico-chemical  
166 parameters of the aquatic environment greatly impact the extent of abiotic methylation. For  
167 example, in Canadian Lakes, DOM having molecular sizes lower than 5 kDa and between 30 kDa  
168 and 300 kDa have been reported to mitigate abiotic methylation occurring through solar irradiation  
169 (Siciliano et al., 2005).

170 Demethylation occurs by multiple and complex processes, which can be mediated by different  
171 biotic and abiotic mechanisms (Barkay and Gu, 2021). Two abiotical processes are commonly  
172 evocated: (i) photochemical demethylation, which is believed to be responsible for a significant

173 part of MeHg degradation in surface waters (Hammerschmidt and Fitzgerald, 2010; Zhang and  
174 Hsu-Kim, 2010); and (ii) chemical demethylation, most likely due to e.g. reaction with H<sub>2</sub>S or  
175 sulfide minerals (Jonsson et al., 2016; Kanzler et al., 2018) and selenoamino acids (Khan and  
176 Wang, 2010). The photodemethylation of MeHg and DMeHg is well-described and considered to  
177 be central in the MeHg degradation in surface waters (Barkay and Gu, 2021). The extent of MeHg  
178 photodemethylation was observed to depend on the type of solar radiation and the concentration  
179 of DOM and structure of MeHg binding sites, which in turn could influence the generation of free  
180 radicals and ROS (e.g. •OH or <sup>1</sup>O<sub>2</sub>) (Hammerschmidt and Fitzgerald, 2006; Lehnher and Louis,  
181 2009; Luo et al., 2020; Sellers et al., 1996). However, there are still some controversies about the  
182 role of DOM in photodemethylation. For example, low DOM concentration promoted, whereas  
183 high DOM concentration inhibited MeHg photodemethylation due to the photons quenching by  
184 DOM (Klapstein and O'Driscoll, 2018). The photodemethylation of MeHg to iHg was shown  
185 increase in the presence of fulvic acids while this process was limited in the presence of humic  
186 acids (Luo et al., 2020). Labile Fe and photochemically produced ROS were shown to play a role  
187 in MeHg photo-decomposition (Hammerschmidt and Fitzgerald, 2010) although demonstrated to  
188 be not compulsory as thiol and phenyl may be the major moieties in DOM-mediated MeHg  
189 photodegradation (Zhang et al., 2018).

190

### 191 ***4.3. Effect of biomolecules on the activity of other organisms***

192 Production of biomolecules by phytoplankton was also shown to affect the Hg transformations  
193 indirectly by affecting mercury methylation by bacteria. For example, organic matter derived from  
194 phytoplankton is considered “a fuel” for methylating organisms and shapes the community  
195 structures of periphytic biofilms (Xing et al., 2018). The symbiotic presence of *Chlorella*  
196 increased the methylation by *Geobacter sulfurreducens* PCA (Zhao et al., 2021). However, the  
197 presence of *Chlorella vulgaris* cells strongly inhibited iHg methylation by *G. anodireducens* SD-  
198 *1* and slightly enhanced iHg methylation by *D. desulfuricans*. Biomolecules released by *Chlorella*

199 had only limited effects on iHg methylation by *G.sulfurreducens* PCA but significantly increased  
200 the MeHg production by *D. desulfuricans* (Yin et al., 2022). A clear positive correlation between  
201 the productivity of methylating microorganisms in sediments and algal productivity was proven  
202 in several aqueous systems (Bravo et al., 2017; Ortega et al., 2018; Wu et al., 2022). However,  
203 further studies are needed since the quality and quantity of the produced biomolecules are species-  
204 specific.

205

## 206 **5. Biotic transformation pathways mediated by phytoplankton**

### 207 **5.1. Biouptake of mercury by phytoplankton species**

208 Biotic transformations of Hg are considered as intracellular processes (Hsu-Kim et al., 2013),  
209 therefore the uptake of iHg and MeHg species by phytoplankton is an important first step in the  
210 overall transformation processes. Nonetheless, the uptake pathways and their kinetics are still not  
211 well understood for phytoplankton species. Evidence are supporting passive diffusion of neutral  
212 charge complexes (Bienvenue et al., 1984; Kim et al., 2014; Mason et al., 1996), facilitated  
213 diffusion (Le Faucheur et al., 2011; Moreno et al., 2014; Wang et al., 2004) as well as possible  
214 active transport pathways (Miles et al., 2001; Moye et al., 2002; Pickhardt and Fisher, 2007).  
215 Passive transport by diatoms, chlorophyte, dinoflagellate, and coccolithophore to acquire MeHg  
216 is considered the most plausible mechanism, related to the surface-area-to-volume ratio of algal  
217 cells (Lee and Fisher, 2016), however, the uptake of MeHg by dinoflagellate *Prorocentrum*  
218 *minimum* was suggested to be an active process.

219 Thiols such as 2-mercaptoethanol, dithiothreitol, and glutathione reduced the uptake of MeHg by  
220 a cyanobacterium, *Nostoc calcicole* (Pant et al., 1995). MeHg uptake by a green alga *Selenastrum*  
221 *capricornutum* was decreased in the presence of cysteine, mercaptoacetic acid, 2-  
222 mercaptopropionic acid, glutathione, *N*-acetyl-L-cysteine and *N*-acetyl-penicillamine (Skrobonja  
223 et al., 2019).

224 The complexation between mercury species and DOM also affects the interactions between Hg

225 and aquatic microorganisms (Brian et al., 2020; Chiasson-Gould et al., 2014; Grégoire et al.,  
226 2018). However, the influence of the EPS on the mercury species' bioavailability is much less  
227 understood. EPS produced by 5 algae (*S. obliquus*, *C. vulgaris*, *C. reinhardtii*, *E. gracilis*, and *E.*  
228 *mutabilis*) were shown to reduce the Hg gene lux induction used as a surrogate for the uptake for  
229 modified *E. coli* but in a way which depends on the species and molecular mass of the EPS: low  
230 molecular mass (LMM) fraction likely participate to bacterial Hg uptake, whereas the highest  
231 molecular mass (HMM) fractions seem to decrease it, for DOM components > 300Da (Mangal et  
232 al., 2019b).

233

## 234 **5.2. Cellular transformations and sequestration of Hg**

235 Phytoplankton was reported to trigger different mercury transformation processes, including  
236 reduction, demethylation, and sequestration of Hg as  $\beta$ -HgS.

### 237 **5.2.1. Cellular reduction and oxidation of mercury species**

238 The reduction of iHg to gaseous Hg<sup>0</sup> has been demonstrated in laboratory experiments with several  
239 phytoplankton species (Grégoire and Poulain, 2014, 2016; Kelly et al., 2006; Mason et al., 1995;  
240 Morelli et al., 2009; Oh et al., 2011; Poulain et al., 2004; Poulain et al., 2007). The volatilization  
241 rates varied between the algal species, Hg concentration and exposure duration (Devars et al.,  
242 2000; Morelli et al., 2009). Early works demonstrated that the exposure of various phytoplankton  
243 species to very high iHg concentrations (Ben-Bassat and Mayer, 1975; Ben-Bassat et al., 1972;  
244 Kelly et al., 2007; Macka et al., 1978; Wilkinson et al., 1989) resulted to Hg<sup>0</sup> production,  
245 observation often linked to the detoxification mechanisms. Diatom *T. weissflogii* was shown to  
246 produce DGM under light and dark conditions suggesting that biological processes rather than  
247 photochemical processes or photosynthetic metabolites mediate this process (Morelli et al., 2009).  
248 Production of DGM was observed for 3 other diatoms species, together with the formation of the  
249 phytochelatin PCs-Hg complexes and  $\beta$ -HgS (Wu and Wang, 2014), suggesting an important role  
250 of intracellular thiols. The reduction of iHg was, however, observed in cultures of *Chlorella*



251 *vulgaris*, but the organic matter released or obtained after cell degradation was shown to reduce  
252 more iHg than living algal cells themselves (Liang et al., 2022). Nevertheless, the fundamental  
253 mechanisms involved in the biological reduction process remain poorly understood.

254 Recent advances revealed the activation of a *MerR*-like transcription factor, Slr0701 when  
255 cyanobacterium *Synechocystis* sp. PCC6803 is exposed to iHg (Singh et al., 2019). The activation  
256 of this transcription factor promotes the expression of the mercuric reductase, MerA-like coded  
257 by the Slr1849 gene, which allows the reduction of iHg into the volatile form Hg<sup>0</sup> (Boyd and  
258 Barkay, 2012; Singh et al., 2019). This process of Hg reduction could enhance the Hg tolerance  
259 of this cyanobacterium. The reduction of iHg to Hg<sup>0</sup> followed by its volatilization is the process  
260 responsible for the evasion of Hg from both terrestrial and aquatic systems (Gonzalez-Raymat et  
261 al., 2017). Hg<sup>0</sup> production by phytoplankton has been thus evidenced in the field (Grégoire and  
262 Poulain, 2014) and the formation of DGM was correlated with phytoplankton dynamics and  
263 blooms (Poulain et al., 2004; Poulain et al., 2007). It was also shown that phototrophic bacteria  
264 use iHg as an electron sink to maintain redox homeostasis to produce Hg<sup>0</sup> (Grégoire and Poulain,  
265 2016). However, it is still unclear whether algae and cyanobacteria are directly involved in DGM  
266 production or if their release of biogenic organic ligands indirectly mediate it.

267

### 268 **5.2.2. Methylation/demethylation of mercury species by phytoplankton**

269 Hg methylation/demethylation by phytoplankton was investigated in the laboratory. For instance,  
270 the potential MeHg demethylation was seen in the cyanobacterium *Nostoc paludosum*, (Franco et  
271 al., 2018), green algae *Chlamydomonas reinhardtii* (Bravo et al., 2014) and four different types  
272 of phytoplankton *Chlorella vulgaris*, *Nostoc* sp., *Microcystis* sp, *Synechocystis* sp. (Yin et al.,  
273 2022), different species of algae (Li et al., 2022), however, no evidences of methylation were  
274 found. Indeed, a specific gene cluster (*hgcAB*) used as a proxy for the microorganism's capability  
275 to methylate iHg (Gilmour et al., 2013), is not found in phytoplankton species. Similarly, no  
276 methylation was observed by pico-nanoplankton from eutrophic lake (Cossart et al., 2021).



277 Although there is no direct evidence that phytoplankton microorganisms can methylate Hg itself,  
278 several studies have highlighted the importance of algae in MeHg production (Lázaro et al., 2019).  
279 Several studies have reported a positive correlation between phototrophic productivity and an  
280 increase in MeHg (Lazaro et al., 2019; Lázaro et al., 2013; Tsui et al., 2010; Xing et al., 2018).  
281 Strong links have been uncovered between methylation rates in open oceans and the presence of  
282 nano- and pico-phytoplankton (Heimbürger et al., 2010). Hg methylation rates were measured at  
283 the maximum chlorophyll depth in oxic surface seawater was measured and influenced by pelagic  
284 microorganism abundance and activities (phyto- and bacterioplankton)(Monperrus et al., 2007).  
285 iHg methylation in the water column was shown to account for around 47% of the MeHg present  
286 in polar marine waters (Lehnherr et al., 2011).

287 Phytoplankton was shown to negatively contribute to methylation rates by sequestering Hg,  
288 retarding its transformation by methylating organisms (Ding et al., 2019). Algal bloom in an  
289 estuary has been thus reported to decrease dissolved MeHg concentration and to increase  
290 particulate MeHg concentration due to algal uptake (Luengen and Flegal, 2009). However, once  
291 phytoplankton dies off, they ultimately sink alongside the accumulated Hg, bringing it to the  
292 anoxic zones enabling the activity of methylators (Coelho et al., 2005). The Hg methylation rates  
293 have been linked with the presence of thiols produced by phytoplankton species and the  
294 decomposition of algal-derived organic matter (Bouchet et al., 2018; Bravo et al., 2017; Zhao et  
295 al., 2021).

296 Demethylation in oxic surface waters has been reported to be partially biologically mediated  
297 besides being induced by solar radiation (Whalin et al., 2007). Reduction and demethylation of  
298 Hg were also demonstrated in the diatom *T. weissflogii* (Devars et al., 2000; Morelli et al., 2009)  
299 and green alga *C. reinhardtii* (Bravo et al., 2014) , diatom *Isochrysis galbana* (Kritee et al., 2017).  
300 However, the transformation yields and demethylation rate constants are still to be elucidated and  
301 quantified. If followed by iHg reduction, phototrophic demethylation is considered a pathway  
302 allowing phototrophs to detoxify Hg species by decreasing cellular Hg concentrations. Very

303 recently, the demethylation capacity of 15 algae species was investigated, and 6 out of 15 species  
304 (dinoflagellates, chrysophytes, and diatoms) tested were able to demethylate MeHg (Li et al.,  
305 2022). The demethylation was also demonstrated in natural pico-nanoplankton communities from  
306 an eutrophic lake (Cossart et al., 2021). Overall, the current understanding of methylation and  
307 demethylation of Hg species by phytoplakton is rather limited. Yet, recent results have highlighted  
308 phytoplanton direct or indirect implications for both processes.

309

### 310 ***5.2.3. Hg intracellular speciation and sequestration by phytoplankton***

311 Phytoplankton species could control intracellular Hg speciation and thus affect the intracellular  
312 transformations by cytosolic ligands. It has been shown that the quantity and the quality of the  
313 intracellular metabolites, which could interact with Hg species, are altered by iHg exposure  
314 (Mangal et al., 2022). Glutathione (GSH), which is the most prevalent thiol in algae, was found  
315 to increase in algae exposed to iHg (Devars et al., 2000; Howe and Merchant, 1992; Morelli et al.,  
316 2009). MeHg exposure was also seen to induce the synthesis of GSH in *Thalassiosira weissflogii*,  
317 but it was iHg that contributed to higher levels of other thiol compounds such as cysteine and PCs  
318 (Wu and Wang, 2012, 2013). More recently, GSH was identified as the main low molecular  
319 weight binding ligand to iHg and MeHg in the cytosolic cyanobacterium *Synechocystis* sp. PCC  
320 6803 (Garcia-Calleja et al., 2021). Phytochelatins (PCs) enzymatically produced from glutathione  
321 are additional thiols used by algae to counteract Hg negative effects (Mehra et al., 1996). For  
322 example, the phytochelatins PC<sub>2,3</sub> have been reported to be synthesized by *T. weissflogii* when  
323 exposed to 5 and 150 nM Hg while MeHg seems to be a poor inducer (Ahner and Morel, 1995;  
324 Howe and Merchant, 1992; Knauer et al., 1998; Morelli et al., 2009). A comparison of  
325 *Thalassiosira weissflogii* with green alga *Chlorella autotrophica* revealed that PCs induction is  
326 highly dependent on the phytoplanktonic species with higher biological responses seen in *T.*  
327 *weissflogii*, and low PCs induction observed for *C. autotrophica* (Wu and Wang, 2014). The  
328 sequestration of iHg binding PCs was identified in the microalga *Chlorella sorokiniana* exposed

329 to high iHg concentrations (Gómez-Jacinto et al., 2015). However, the role of these thiols in  
330 cellular iHg and MeHg transformations still needs to be confirmed under lower environmentally  
331 realistic exposure Hg concentrations.

332 Hg sequestration as  $\beta$ -HgS has been demonstrated as a detoxification mechanism in a variety of  
333 cyanobacteria *Limnothrix planctonica*, *Synechococcus leopoldiensis*, and *Phormidium limnetica*  
334 (Kelly et al., 2006; Kelly et al., 2007). Green algae *Chlorella autotrophica*, flagellate *Isochrysis*  
335 *galbana*, and marine diatom *Thalassiosira weissflogii*) could transform iHg into cinnabar ( $\beta$ -HgS)  
336 (Wu and Wang, 2014). The sunlight was also shown to facilitate the transformation of Hg to less  
337 bioavailable species, such as  $\beta$ -HgS and Hg-phytochelatins (Liang et al., 2022). Overall,  
338 phytoplankton can sequester high quantities of Hg as a detoxification strategy without apparent  
339 harmful effects. The tolerance to Hg species toxicity has been related to the capacity of the  
340 phytoplankton to capture Hg in subcellular compartments as vacuoles which serve as a sink for  
341 mineralized form or LMW thiol compounds. Nevertheless, no information has been ever provided  
342 at environmentally relevant concentrations.

343  
344 The examples presented above demonstrated the important role of thiol-compounds in  
345 intracellular handling of iHg and MeHg and the existing research gaps in understanding the  
346 underlying mechanisms and interplay between iHg and MeHg transformation and thiol-pathways.  
347 The lack of tailored analytical methods for thiols identification and quantification has until now  
348 precluded experiments to investigate their influence on Hg accumulation. However, the recent  
349 developments allowing direct quantification of both LMW and HMW thiols and their Hg  
350 complexes (Garcia-Calleja et al., 2021; Pedrero et al., 2011; Pedrero Zayas et al., 2014), open new  
351 opportunities for exploring the role of intra- and extracellular ligands in Hg uptake and biotic  
352 transformation. On the other hand, the exposure of *Chlamydomonas reinhardtii* to low (50 nM )  
353 and high (5 nM) iHg and MeHg concentrations induced metabolic perturbations in amino acid and  
354 nucleotide synthesis and degradation, fatty acids, carbohydrates, tricarboxylic acid, antioxidants

355 and photorespiration (Slaveykova et al., 2021).

356

## 357 **6. Conclusion and perspectives**

358 Important research advances confirmed that phytoplankton could affect Hg speciation and  
359 transformations directly e.g. via biotic transformations of the accumulated mercury species and/or  
360 indirectly via the release of low and high molecular mass molecules which could complex mercury  
361 and affect both abiotic and biotic transformations of Hg compounds. The up-to-date studies  
362 revealed that different microalgal species and cyanobacteria contribute to iHg biotic reduction into  
363 Hg<sup>0</sup>, as well as MeHg demethylation and transformation of iHg into metacinnabar, as well as  
364 produce different biomolecules which can contribute to abiotic mercury reduction. Numerous  
365 questions remain open concerning the underlying mechanisms of Hg species interactions with  
366 phytoplankton in terms of their uptake mechanisms and cellular handling, including the release of  
367 biomolecules, which will be the focus of future research.

368 The role of the phytoplankton in biotic transformations of mercury species and their significance  
369 compared to other microorganisms such as bacteria are overlooked and need to be further  
370 explored. Therefore, further studies which quantitatively examine different transformation  
371 processes and identify the phytoplankton species or groups of species able to demethylate or  
372 reduce mercury in situ are highly sought.

373 The development and application of novel state-of-the-art techniques would greatly facilitate such  
374 studies. The development of the Hg stable isotope fractionation approach opens up the possibility  
375 to decipher further the contribution of interconnected abiotic and biotic transformation (Kritee et  
376 al., 2013). Since the biotic transformations are considered prevailing, the development of the new  
377 -omics approaches would provide key information on the interactions between Hg and  
378 phytoplankton species (Beauvais-Flück et al., 2018; Beauvais-Flück et al., 2016; Mangal et al.,  
379 2022; Slaveykova et al., 2021).

380 The understanding of the cellular transformations and speciation is central for the elucidation of

381 the role of phytoplankton in Hg biogeochemical cycles and is of high importance to better predict  
382 the long-term changes in Hg bioavailability to food webs. Indeed, a global circulation 3D model  
383 of MeHg in seawater showed that diatoms and picocyanobacterium *Synechococcus* spp. are the  
384 most important phytoplankton categories for the transfer of MeHg from seawater to herbivorous  
385 zooplankton, contributing 35% and 25%, respectively (Zhang et al., 2020).

386 Given the interconnection between the global change and biogeochemical cycling of mercury  
387 (Chetelat et al., 2022), a deeper understanding of the mercury transformation processes triggered  
388 by phytoplankton, measured both in the laboratory and in situ and the development of mechanistic  
389 models coupling primary production, Hg transport, and transformations and climate models  
390 would allow projections under various climate change scenarios at a global scale. This will further  
391 constrain the efficiency of the measures taken by the Minamata convention to reduce mercury  
392 emissions. This is important given continuous anthropogenic Hg inputs to aquatic ecosystems and  
393 considerable shifts in the phytoplankton dynamics predicted with global change.

#### 394 **Data Availability Statement**

395 Data sharing is not applicable as no new data were generated or analyzed during this study.

#### 396 **Conflicts of Interest**

397 The authors declare no conflicts of interest.

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#### 401 **References**

- 402 Ahner, B.A., Morel, F.M.M., 1995. Phytochelatin production In marine-Algae .2. Induction by  
403 various metals. *Limnology and Oceanography* 40, 658-665.  
404 Amyot, M., Gill, G.A., Morel, F.M.M., 1997. Production and Loss of Dissolved Gaseous Mercury  
405 in Coastal Seawater. *Environmental Science & Technology* 31, 3606-3611.  
406 Ariya, P.A., Amyot, M., Dastoor, A., Deeds, D., Feinberg, A., Kos, G., Poulain, A., Ryjkov, A.,  
407 Semeniuk, K., Subir, M., Toyota, K., 2015. Mercury Physicochemical and Biogeochemical  
408 Transformation in the Atmosphere and at Atmospheric Interfaces: A Review and Future

- 409 Directions. Chemical Reviews 115, 3760-3802.
- 410 Asaduzzaman, A., Riccardi, D., Afaneh, A.T., Cooper, C.J., Smith, J.C., Wang, F., Parks, J.M.,  
411 Schreckenbach, G., 2019. Environmental Mercury Chemistry – In Silico. Accounts of  
412 Chemical Research 52, 379-388.
- 413 Babiak, W., Krzemińska, I., 2021. Extracellular Polymeric Substances (EPS) as Microalgal  
414 Bioproducts: A Review of Factors Affecting EPS Synthesis and Application in Flocculation  
415 Processes. Energies 14, 4007.
- 416 Barkay, T., Gu, B., 2021. Demethylation— The Other Side of the Mercury Methylation Coin: A  
417 Critical Review. ACS Environmental Au.
- 418 Beauvais-Flück, R., Slaveykova, V., Cosio, C., 2018. Molecular Effects of Inorganic and Methyl  
419 Mercury in Aquatic Primary Producers: Comparing Impact to A Macrophyte and A Green  
420 Microalga in Controlled Conditions. Geosciences 8, 393.
- 421 Beauvais-Flück, R., Slaveykova, V.I., Cosio, C., 2016. Transcriptomic and Physiological  
422 Responses of the Green Microalga *Chlamydomonas reinhardtii* during Short-Term  
423 Exposure to Subnanomolar Methylmercury Concentrations. Environmental Science &  
424 Technology 50, 7126-7134.
- 425 Ben-Bassat, D., Mayer, A.M., 1975. Volatilization of Mercury by Algae. Physiologia Plantarum  
426 33, 128-132.
- 427 Ben-Bassat, D., Shelef, G., Gruner, N., Shuval, H.I., 1972. Growth of *Chlamydomonas* in a  
428 medium containing mercury. Nature 240, 43-44.
- 429 Bienvenue, E., Boudou, A., Desmazes, J.P., Gavach, C., Georgescauld, D., Sandeaux, J.,  
430 Sandeaux, R., Seta, P., 1984. Transport of mercury compounds across bimolecular lipid  
431 membranes: effect of lipid composition, pH and chloride concentration. Chemo-  
432 Biological Interactions 48, 91-101.
- 433 Black, F.J., Poulin, B.A., Flegal, A.R., 2012. Factors controlling the abiotic photo-degradation of  
434 monomethylmercury in surface waters. Geochimica et Cosmochimica Acta 84, 492-507.
- 435 Bouchet, S., Björn, E., 2014. Analytical developments for the determination of  
436 monomethylmercury complexes with low molecular mass thiols by reverse phase liquid  
437 chromatography hyphenated to inductively coupled plasma mass spectrometry. Journal of  
438 Chromatography A 1339, 50-58.
- 439 Bouchet, S., Goñi-Urriza, M., Monperrus, M., Guyoneaud, R., Fernandez, P., Heredia, C., Tessier,  
440 E., Gassie, C., Point, D., Guédron, S., Achá, D., Amouroux, D., 2018. Linking Microbial  
441 Activities and Low-Molecular-Weight Thiols to Hg Methylation in Biofilms and Periphyton  
442 from High-Altitude Tropical Lakes in the Bolivian Altiplano. Environmental Science &  
443 Technology 52, 9758-9767.
- 444 Boyd, E., Barkay, T., 2012. The Mercury Resistance Operon: From an Origin in a Geothermal  
445 Environment to an Efficient Detoxification Machine. Frontiers in Microbiology 3.
- 446 Branfireun, B.A., Cosio, C., Poulain, A.J., Riise, G., Bravo, A.G., 2020. Mercury cycling in  
447 freshwater systems - An updated conceptual model. Sci Total Environ 745, 140906.
- 448 Bravo, A.G., Bouchet, S., Tolu, J., Bjorn, E., Mateos-Rivera, A., Bertilsson, S., 2017. Molecular  
449 composition of organic matter controls methylmercury formation in boreal lakes. Nature  
450 Communications 8.
- 451 Bravo, A.G., Le Faucheur, S., Monperrus, M., Amouroux, D., Slaveykova, V.I., 2014. Species-  
452 specific isotope tracers to study the accumulation and biotransformation of mixtures of  
453 inorganic and methyl mercury by the microalga *Chlamydomonas reinhardtii*. Environ Pollut  
454 192, 212-215.
- 455 Brian, A.B., Claudia, C., Alexandre, J.P., Gunnhild, R., Andrea, G.B., 2020. Mercury cycling in  
456 freshwater systems - An updated conceptual model. Science of The Total Environment 745,  
457 140906.
- 458 Celso, V., Lean, D.R., Scott, S.L., 2006. Abiotic methylation of mercury in the aquatic  
459 environment. Sci Total Environ 368, 126-137.



- 460 Chen, H.W., Huang, W.J., Wu, T.H., Hon, C.L., 2014. Effects of extracellular polymeric  
461 substances on the bioaccumulation of mercury and its toxicity toward the cyanobacterium  
462 *Microcystis aeruginosa*. *Journal of Environmental Science and Health Part a-*  
463 *Toxic/Hazardous Substances & Environmental Engineering* 49, 1370-1379.
- 464 Chen, W.B., Smith, D.S., Guéguen, C., 2013. Influence of water chemistry and dissolved organic  
465 matter (DOM) molecular size on copper and mercury binding determined by multiresponse  
466 fluorescence quenching. *Chemosphere* 92, 351-359.
- 467 Chetelat, J., McKinney, M.A., Amyot, M., Dastoor, A., Douglas, T.A., Heimbürger-Boavida,  
468 L.E., Kirk, J., Kahilainen, K.K., Outridge, P.M., Pelletier, N., Skov, H., St Pierre, K.,  
469 Vuorenmaa, J., Wang, F.Y., 2022. Climate change and mercury in the Arctic: Abiotic  
470 interactions. *Science of The Total Environment* 824.
- 471 Chiasson-Gould, S.A., Blais, J.M., Poulain, A.J., 2014. Dissolved Organic Matter Kinetically  
472 Controls Mercury Bioavailability to Bacteria. *Environmental Science & Technology* 48,  
473 3153-3161.
- 474 Coelho, J., Pereira, M., Duarte, A., Pardal, M., 2005. Macroalgae response to a mercury  
475 contamination gradient in a temperate coastal lagoon (Ria de Aveiro, Portugal). *Estuarine,  
476 Coastal and Shelf Science* 65, 492-500.
- 477 Cossart, T., Garcia-Calleja, J., Worms, I.A.M., Tessier, E., Kavanagh, K., Pedrero, Z., Amouroux,  
478 D., Slaveykova, V.I., 2021. Species-specific isotope tracking of mercury uptake and  
479 transformations by pico-nanoplankton in an eutrophic lake. *Environmental Pollution* 288,  
480 117771.
- 481 Devars, S., Avilés, C., Cervantes, C., Moreno-Sánchez, R., 2000. Mercury uptake and removal by  
482 *Euglena gracilis*. *Archives of Microbiology* 174, 175-180.
- 483 Ding, L.Y., Zhang, Y.Y., Zhang, L.J., Fang, F., He, N.N., Liang, P., Wu, S.C., Wong, M.H., Tao,  
484 H.C., 2019. Mercury methylation by *Geobacter metallireducens* GS-15 in the presence of  
485 *Skeletonema costatum*. *Sci Total Environ* 671, 208-214.
- 486 Dranguet, P., Flück, R., Regier, N., Cosio, C., Le Faucheur, S., Slaveykova, V.I., 2014. Towards  
487 Mechanistic Understanding of Mercury Availability and Toxicity to Aquatic Primary  
488 Producers. *CHIMIA International Journal for Chemistry* 68, 799-805.
- 489 Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global  
490 pollutant: sources, pathways, and effects. *Environ Sci Technol* 47, 4967-4983.
- 491 Du, H.X., Ma, M., Igarashi, Y., Wang, D.Y., 2019. Biotic and Abiotic Degradation of  
492 Methylmercury in Aquatic Ecosystems: A Review. *Bulletin of Environmental  
493 Contamination and Toxicology* 102, 605-611.
- 494 Franco, M.W., Mendes, L.A., Windmöller, C.C., Moura, K.A.F., Oliveira, L.A.G., Barbosa,  
495 F.A.R., 2018. Mercury Methylation Capacity and Removal of Hg Species from Aqueous  
496 Medium by Cyanobacteria. *Water, Air, & Soil Pollution* 229.
- 497 Gallorini, A., Loizeau, J.L., 2021. Mercury methylation in oxic aquatic macro-environments: a  
498 review. *Journal of Limnology* 80.
- 499 Garcia-Calleja, J., Cossart, T., Pedrero, Z., Santos, J.P., Ouerdane, L., Tessier, E., Slaveykova,  
500 V.I., Amouroux, D., 2021. Determination of the Intracellular Complexation of Inorganic  
501 and Methylmercury in Cyanobacterium *Synechocystis* sp. PCC 6803. *Environmental  
502 Science & Technology* 55, 13971-13979.
- 503 Ghimire, P.S., Tripathee, L., Zhang, Q.G., Guo, J.M., Ram, K., Huang, J., Sharma, C.M., Kang,  
504 S.C., 2019. Microbial mercury methylation in the cryosphere: Progress and prospects.  
505 *Science of The Total Environment* 697.
- 506 Gilmour, C.C., Podar, M., Bullock, A.L., Graham, A.M., Brown, S.D., Somenahally, A.C., Johs,  
507 A., Hurt, R.A., Jr., Bailey, K.L., Elias, D.A., 2013. Mercury methylation by novel  
508 microorganisms from new environments. *Environ Sci Technol* 47, 11810-11820.
- 509 Gómez-Jacinto, V., García-Barrera, T., Gómez-Ariza, J.L., Garbayo-Nores, I., Vilchez-Lobato,  
510 C., 2015. Elucidation of the defence mechanism in microalgae *Chlorella sorokiniana* under

- 511 mercury exposure. Identification of Hg–phytochelatins. *Chemico-Biological Interactions*  
512 238, 82-90.
- 513 Gonzalez-Raymat, H., Liu, G., Liriano, C., Li, Y., Yin, Y., Shi, J., Jiang, G., Cai, Y., 2017.  
514 Elemental mercury: Its unique properties affect its behavior and fate in the environment.  
515 *Environmental Pollution* 229, 69-86.
- 516 Grégoire, D.S., Poulain, A.J., 2014. A little bit of light goes a long way: the role of phototrophs  
517 on mercury cycling. *Metallomics* 6, 396-407.
- 518 Grégoire, D.S., Poulain, A.J., 2016. A physiological role for HgII during phototrophic growth.  
519 *Nature Geoscience* 9, 121-125.
- 520 Grégoire, D.S., Poulain, A.J., Ivanova, E.P., 2018. Shining light on recent advances in microbial  
521 mercury cycling. *Facets* 3, 858-879.
- 522 Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Photodecomposition of methylmercury in an arctic  
523 Alaskan lake. *Environmental Science & Technology* 40, 1212-1216.
- 524 Hammerschmidt, C.R., Fitzgerald, W.F., 2010. Iron-mediated photochemical decomposition of  
525 methylmercury in an arctic Alaskan lake. *Environ Sci Technol* 44, 6138-6143.
- 526 Heimbürger, L.-E., Cossa, D., Marty, J.-C., Migon, C., Averty, B., Dufour, A., Ras, J., 2010.  
527 Methyl mercury distributions in relation to the presence of nano- and picophytoplankton in  
528 an oceanic water column (Ligurian Sea, North-western Mediterranean). *Geochimica et*  
529 *Cosmochimica Acta* 2010, 5549-5559.
- 530 Howe, G., Merchant, S., 1992. Heavy metal-activated synthesis of peptides in *Chlamydomonas*  
531 *reinhardtii*. *Plant Physiology* 98, 127-136.
- 532 Hsu-Kim, H., Kucharzyk, K.H., Zhang, T., Deshusses, M.A., 2013. Mechanisms Regulating  
533 Mercury Bioavailability for Methylating Microorganisms in the Aquatic Environment: A  
534 Critical Review. *Environmental Science & Technology* 47, 2441-2456.
- 535 Jiang, T., Skjellberg, U., Björn, E., Green, N.W., Tang, J., Wang, D., Gao, J., Li, C., 2017.  
536 Characteristics of dissolved organic matter (DOM) and relationship with dissolved mercury  
537 in Xiaoqing River-Laizhou Bay estuary, Bohai Sea, China. *Environmental Pollution* 223,  
538 19-30.
- 539 Jiskra, M., Heimbürger-Boavida, L.E., Desgranges, M.M., Petrova, M.V., Dufour, A., Ferreira-  
540 Araujo, B., Masbou, J., Chmeleff, J., Thyssen, M., Point, D., Sonke, J.E., 2021. Mercury  
541 stable isotopes constrain atmospheric sources to the ocean. *Nature* 597, 678-682.
- 542 Jiskra, M., Wiederhold, J.G., Skjellberg, U., Kronberg, R.-M., Kretzschmar, R., 2017. Source  
543 tracing of natural organic matter bound mercury in boreal forest runoff with mercury stable  
544 isotopes. *Environmental Science: Processes & Impacts* 19, 1235-1248.
- 545 Jonsson, S., Mazrui, N.M., Mason, R.P., 2016. Dimethylmercury formation mediated by inorganic  
546 and organic reduced sulfur surfaces. *Scientific Reports* 6, 1-7.
- 547 Kanzler, C.R., Lian, P., Trainer, E.L., Yang, X., Govind, N., Parks, J.M., Graham, A.M., 2018.  
548 Emerging investigator series: methylmercury speciation and dimethylmercury production  
549 in sulfidic solutions. *Environmental Science: Processes & Impacts* 20, 584-594.
- 550 Kelly, D., Budd, K., Lefebvre, D.D., 2006. Mercury analysis of acid- and alkaline-reduced  
551 biological samples: Identification of meta-cinnabar as the major biotransformed compound  
552 in algae. *Applied and Environmental Microbiology* 72, 361-367.
- 553 Kelly, D.J., Budd, K., Lefebvre, D.D., 2007. Biotransformation of mercury in pH-stat cultures of  
554 eukaryotic freshwater algae. *Archives of Microbiology* 187, 45-53.
- 555 Khan, M.A.K., Wang, F., 2010. Chemical Demethylation of Methylmercury by Selenoamino  
556 Acids. *Chemical Research in Toxicology* 23, 1202-1206.
- 557 Kim, H., Van Duong, H., Kim, E., Lee, B.G., Han, S., 2014. Effects of phytoplankton cell size  
558 and chloride concentration on the bioaccumulation of methylmercury in marine  
559 phytoplankton. *Environ Toxicol* 29, 936-941.
- 560 Klapstein, S.J., O'Driscoll, N.J., 2018. Methylmercury Biogeochemistry in Freshwater  
561 Ecosystems: A Review Focusing on DOM and Photodemethylation. *Bulletin of*



- 562 Environmental Contamination and Toxicology 100, 14-25.
- 563 Knauer, K., Ahner, B., Xue, H.B., Sigg, L., 1998. Metal and phytochelatin content in  
564 phytoplankton from freshwater lakes with different metal concentrations. Environmental  
565 Toxicology and Chemistry 17, 2444-2452.
- 566 Kritee, K., Blum, J.D., Reinfelder, J.R., Barkay, T., 2013. Microbial stable isotope fractionation  
567 of mercury: A synthesis of present understanding and future directions. Chemical Geology  
568 336, 13-25.
- 569 Lalonde, J.D., Amyot, M., Kraepiel, A.M., Morel, F.M., 2001. Photooxidation of Hg(0) in  
570 artificial and natural waters. Environ Sci Technol 35, 1367-1372.
- 571 Lamborg, C.H., Fitzgerald, W.F., Skoog, A., Visscher, P.T., 2004. The abundance and source of  
572 mercury-binding organic ligands in Long Island Sound. Marine Chemistry 90, 151-163.
- 573 Lanzillotta, E., Ceccarini, C., Ferrara, R., Dini, F., Frontini, F.P., Banchetti, R., 2004. Importance  
574 of the biogenic organic matter in photo-formation of dissolved gaseous mercury in a culture  
575 of the marine diatom *Chaetoceros* sp. Science of The Total Environment 318, 211-221.
- 576 Lavoie, R.A., Amyot, M., Lapierre, J.-F., 2019. Global Meta-Analysis on the Relationship  
577 Between Mercury and Dissolved Organic Carbon in Freshwater Environments. Journal of  
578 Geophysical Research: Biogeosciences 124, 1508-1523.
- 579 Lazaro, W.L., Díez, S., Bravo, A.G., da Silva, C.J., Ignacio, A.R.A., Guimaraes, J.R.D., 2019.  
580 Cyanobacteria as regulators of methylmercury production in periphyton. Sci Total Environ  
581 668, 723-729.
- 582 Lázaro, W.L., Guimarães, J.R.D., Ignácio, A.R.A., Da Silva, C.J., Díez, S., 2013. Cyanobacteria  
583 enhance methylmercury production: A hypothesis tested in the periphyton of two lakes in  
584 the Pantanal floodplain, Brazil. Science of The Total Environment 456-457, 231-238.
- 585 Le Faucheur, S., Campbell, P.G., Fortin, C., Slaveykova, V.I., 2014. Interactions between mercury  
586 and phytoplankton: speciation, bioavailability, and internal handling. Environ Toxicol  
587 Chem 33, 1211-1224.
- 588 Le Faucheur, S., Fortin, C., Campbell, P.G.C., 2011. Acidification increases mercury uptake by a  
589 freshwater alga, *Chlamydomonas reinhardtii*. Environmental Chemistry 8, 612-622.
- 590 Lee, C.S., Fisher, N.S., 2016. Methylmercury uptake by diverse marine phytoplankton. Limnol  
591 Oceanogr 61, 1626-1639.
- 592 Lehnherr, I., Louis, V.L.S., 2009. Importance of Ultraviolet Radiation in the Photodemethylation  
593 of Methylmercury in Freshwater Ecosystems. Environmental Science & Technology 43,  
594 5692-5698.
- 595 Lehnherr, I., St. Louis, V.L., Hintelmann, H., Kirk, J.L., 2011. Methylation of inorganic mercury  
596 in polar marine waters. Nature Geoscience 4, 298-302.
- 597 Li, Y., Li, D., Song, B., Li, Y., 2022. The potential of mercury methylation and demethylation by  
598 15 species of marine microalgae. Water Research 215.
- 599 Liang, X., Zhu, N., Johs, A., Chen, H., Pelletier, D.A., Zhang, L., Yin, X., Gao, Y., Zhao, J., Gu,  
600 B., 2022. Mercury Reduction, Uptake, and Species Transformation by Freshwater Alga  
601 *Chlorella vulgaris* under Sunlit and Dark Conditions. Environ Sci Technol.
- 602 Liem-Nguyen, V., Bouchet, S., Björn, E., 2015. Determination of Sub-Nanomolar Levels of Low  
603 Molecular Mass Thiols in Natural Waters by Liquid Chromatography Tandem Mass  
604 Spectrometry after Derivatization with p-(Hydroxymercuri) Benzoate and Online  
605 Preconcentration. Analytical Chemistry 87, 1089-1096.
- 606 Liem-Nguyen, V., Skyllberg, U., Björn, E., 2017. Thermodynamic Modeling of the Solubility and  
607 Chemical Speciation of Mercury and Methylmercury Driven by Organic Thiols and  
608 Micromolar Sulfide Concentrations in Boreal Wetland Soils. Environmental Science &  
609 Technology 51, 3678-3686.
- 610 Liu, F., Tan, Q.-G., Weiss, D., Crémazy, A., Fortin, C., Campbell, P.G.C., 2020. Unravelling  
611 Metal Speciation in the Microenvironment Surrounding Phytoplankton Cells to Improve  
612 Predictions of Metal Bioavailability. Environmental Science & Technology 54, 8177-8185.

- 613 Luengen, A.C., Flegal, A.R., 2009. Role of phytoplankton in mercury cycling in the San Francisco  
614 Bay estuary. *Limnology and Oceanography* 54, 23-40.
- 615 Luo, H., Cheng, Q., Pan, X., 2020. Photochemical behaviors of mercury (Hg) species in aquatic  
616 systems: A systematic review on reaction process, mechanism, and influencing factor.  
617 *Science of The Total Environment* 720, 137540.
- 618 Ly, Q.V., Maqbool, T., Hur, J., 2017. Unique characteristics of algal dissolved organic matter and  
619 their association with membrane fouling behavior: a review. *Environmental Science and*  
620 *Pollution Research* 24, 11192-11205.
- 621 Macka, W., Wihlidal, H., Stehlik, G., Washuttl, J., Bancher, E., 1978. Metabolic studies of Hg-  
622 203 on *Chlamydomonas reinhardi*. *Experientia* 34, 602-603.
- 623 Mangal, V., Donaldson, M.E., Lewis, A., Saville, B.J., Guéguen, C., 2022. Identifying *Euglena*  
624 *Gracilis* Metabolic and Transcriptomic Adaptations in Response to Mercury Stress.  
625 *Frontiers in Environmental Science* 10.
- 626 Mangal, V., Phung, T., Nguyen, T.Q., Guéguen, C., 2019a. Molecular Characterization of  
627 Mercury Binding Ligands Released by Freshwater Algae Grown at Three Photoperiods.  
628 *Frontiers in Environmental Science* 6.
- 629 Mangal, V., Stenzler, B.R., Poulain, A.J., Guéguen, C., 2019b. Aerobic and Anaerobic Bacterial  
630 Mercury Uptake is Driven by Algal Organic Matter Composition and Molecular Weight.  
631 *Environmental Science & Technology* 53, 157-165.
- 632 Mangal, V., Stock, N.L., Gueguen, C., 2016. Molecular characterization of phytoplankton  
633 dissolved organic matter (DOM) and sulfur components using high resolution Orbitrap mass  
634 spectrometry. *Analytical and Bioanalytical Chemistry* 408, 1891-1900.
- 635 Mason, R.P., Morel, F.M.M., Hemond, H.F., 1995. The role of microorganisms in elemental  
636 mercury formation in natural waters. *Water Air And Soil Pollution* 80, 775-787.
- 637 Mason, R.P., Reinfelder, J.R., Morel, F.M.M., 1996. Uptake, toxicity, and trophic transfer of  
638 mercury in a coastal diatom. *Environmental Science and Technology* 30, 1835-1845.
- 639 Mehra, R.K., Miclat, J., Kodati, R., Abdullah, R., Hunter, T.C., Mulchandani, P., 1996. Optical  
640 spectroscopic and revers-phase HPLC analysis of Hg<sup>2+</sup> binding to phytochelatins. *Biochem*  
641 *J* 314, 73-82.
- 642 Miles, C.J., Moye, H.A., Philips, E.J., Sargent, B., 2001. Partitioning of monomethylmercury  
643 between freshwater algae and water. *Environmental Science & Technology* 35, 4277-4282.
- 644 Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., Donard, O.F.X., 2007.  
645 Mercury methylation, demethylation and reduction rates in coastal and marine surface  
646 waters of the Mediterranean Sea. *Marine Chemistry* 107, 49-63.
- 647 Morelli, E., Ferrara, R., Bellini, B., Dini, F., Di Giuseppe, G., Fantozzi, L., 2009. Changes in the  
648 non-protein thiol pool and production of dissolved gaseous mercury in the marine diatom  
649 *Thalassiosira weissflogii* under mercury exposure. *Science of The Total Environment* 408,  
650 286-293.
- 651 Moreno, F., Garcia-Barrera, T., Gomez-Jacinto, V., Gomez-Ariza, J.L., Garbayo-Nores, I.,  
652 Vilchez-Lobato, C., 2014. Antagonistic interaction of selenomethionine enantiomers on  
653 methylmercury toxicity in the microalgae *Chlorella sorokiniana*. *Metallomics* 6, 347-355.
- 654 Moye, H.A., Miles, C.J., Philips, E.J., Sargent, B., Merritt, K.K., 2002. Kinetics and uptake  
655 mechanisms for monomethylmercury between freshwater algae and water. *Environmental*  
656 *Science and Technology* 36, 3550-3555.
- 657 Naveed, S., Li, C.H., Lu, X.D., Chen, S.S., Yin, B., Zhang, C.H., Ge, Y., 2019. Microalgal  
658 extracellular polymeric substances and their interactions with metal(loid)s: A review.  
659 *Critical Reviews in Environmental Science and Technology* 49, 1769-1802.
- 660 Oh, S., Kim, M.-K., Lee, Y.-M., Zoh, K.-D., 2011. Effect of Abiotic and Biotic Factors on the  
661 Photo-Induced Production of Dissolved Gaseous Mercury. *Water, Air, & Soil Pollution* 220,  
662 353-363.
- 663 Ortega, S.H., Catalan, N., Bjorn, E., Grontoft, H., Hilmarsson, T.G., Bertilsson, S., Wu, P.P.,

- 664 Bishop, K., Levanoni, O., Bravo, A.G., 2018. High methylmercury formation in ponds  
665 fueled by fresh humic and algal derived organic matter. *Limnology and Oceanography* 63,  
666 S44-S53.
- 667 Pant, A., Srivastava, S.C., Singh, S.P., 1995. Factors Regulating Methyl Mercury Uptake in a  
668 Cyanobacterium. *Ecotoxicology and Environmental Safety* 32, 87-92.
- 669 Paranjape, A.R., Hall, B.D., 2017. Recent advances in the study of mercury methylation in aquatic  
670 systems. *Facets* 2.
- 671 Pedrero, Z., Mounicou, S., Monperrus, M., Amouroux, D., 2011. Investigation of Hg species  
672 binding biomolecules in dolphin liver combining GC and LC-ICP-MS with isotopic tracers.  
673 *Journal of Analytical Atomic Spectrometry* 26, 187-194.
- 674 Pedrero Zayas, Z., Ouerdane, L., Mounicou, S., Lobinski, R., Monperrus, M., Amouroux, D.,  
675 2014. Hemoglobin as a major binding protein for methylmercury in white-sided dolphin  
676 liver. *Analytical and Bioanalytical Chemistry* 406, 1121-1129.
- 677 Pickhardt, P.C., Fisher, N.S., 2007. Accumulation of inorganic and methylmercury by freshwater  
678 phytoplankton in two contrasting water bodies. *Environmental Science and Technology* 41,  
679 125-131.
- 680 Poulain, A.J., Amyot, M., Findlay, D., Telor, S., Barkay, T., Hintelmann, H., 2004. Biological and  
681 photochemical production of dissolved gaseous mercury in a boreal lake. *Limnology and*  
682 *Oceanography* 49, 2265-2275.
- 683 Poulain, A.J., Garcia, E., Amyot, M., Campbell, P.G.C., Raofie, F., Ariya, P.A., 2007. Biological  
684 and chemical redox transformations of mercury in fresh and salt waters of the high arctic  
685 during spring and summer. *Environmental Science & Technology* 41, 1883-1888.
- 686 Poulin, B.A., Ryan, J.N., Tate, M.T., Krabbenhoft, D.P., Hines, M.E., Barkay, T., Schaefer, J.,  
687 Aiken, G.R., 2019. Geochemical Factors Controlling Dissolved Elemental Mercury and  
688 Methylmercury Formation in Alaskan Wetlands of Varying Trophic Status. *Environmental*  
689 *Science & Technology* 53, 6203-6213.
- 690 Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter--a review.  
691 *Chemosphere* 55, 319-331.
- 692 Sellers, P., Kelly, C.A., Rudd, J.W.M., MacHutchon, A.R., 1996. Photodegradation of  
693 methylmercury in lakes. *Nature* 380, 694-697.
- 694 Seymour, J.R., Amin, S.A., Raina, J.-B., Stocker, R., 2017. Zooming in on the phycosphere: the  
695 ecological interface for phytoplankton–bacteria relationships. *Nature Microbiology* 2,  
696 17065.
- 697 Sheehan, M.C., Burke, T.A., Navas-Acien, A., Breyse, P.N., McGready, J., Fox, M.A., 2014.  
698 Global methylmercury exposure from seafood consumption and risk of developmental  
699 neurotoxicity: a systematic review. *Bulletin of the World Health Organization* 92, 254-269F.
- 700 Shou, W., Kang, F., Lu, J., 2018. Nature and Value of Freely Dissolved EPS Ecosystem Services:  
701 Insight into Molecular Coupling Mechanisms for Regulating Metal Toxicity. *Environmental*  
702 *Science & Technology* 52, 457-466.
- 703 Siciliano, S.D., O'Driscoll, N.J., Tordon, R., Hill, J., Beauchamp, S., Lean, D.R.S., 2005. Abiotic  
704 production of methylmercury by solar radiation. *Environmental Science & Technology* 39,  
705 1071-1077.
- 706 Singh, D.K., Lingaswamy, B., Koduru, T.N., Nagu, P.P., Jogadhenu, P.S.S., 2019. A putative  
707 merR family transcription factor Slr0701 regulates mercury inducible expression of MerA  
708 in the cyanobacterium *Synechocystis* sp. PCC6803. *MicrobiologyOpen* 8, e00838.
- 709 Skrobonja, A., Gojkovic, Z., Soerensen, A.L., Westlund, P.-O., Funk, C., Björn, E., 2019. Uptake  
710 Kinetics of Methylmercury in a Freshwater Alga Exposed to Methylmercury Complexes  
711 with Environmentally Relevant Thiols. *Environmental Science & Technology* 53, 13757-  
712 13766.
- 713 Slaveykova, V.I., Majumdar, S., Regier, N., Li, W., Keller, A.A., 2021. Metabolomic Responses  
714 of Green Alga *Chlamydomonas reinhardtii* Exposed to Sublethal Concentrations of

- 715 Inorganic and Methylmercury. *Environmental Science & Technology* 55, 3876-3887.
- 716 Song, W.J., Pan, X.L., Mu, S.Y., Zhang, D.Y., Yang, X., Lee, D.J., 2014. Biosorption of Hg(II)
- 717 onto goethite with extracellular polymeric substances. *Bioresource Technology* 160, 119-
- 718 122.
- 719 Tai, C., Li, Y., Yin, Y., Scinto, L.J., Jiang, G., Cai, Y., 2014. Methylmercury Photodegradation in
- 720 Surface Water of the Florida Everglades: Importance of Dissolved Organic Matter-
- 721 Methylmercury Complexation. *Environmental Science & Technology* 48, 7333-7340.
- 722 Tsui, M.T., Finlay, J.C., Balogh, S.J., Nollet, Y.H., 2010. In situ production of methylmercury
- 723 within a stream channel in northern California. *Environ Sci Technol* 44, 6998-7004.
- 724 Vasconcelos, M.T.S.D., Leal, M.F.C., van den Berg, C.M.G., 2002. Influence of the nature of the
- 725 exudates released by different marine algae on the growth, trace metal uptake, and exudation
- 726 of *Emiliana huxleyi* in natural seawater. *Marine Chemistry* 77, 187-210.
- 727 Vost, E.E., Amyot, M., O'Driscoll, N.J., 2012. Photoreactions of mercury in aquatic systems, in:
- 728 Liu, G.L., Cai, Y., O'Driscoll, N.J. (Eds.), *Environmental Chemistry and Toxicology of*
- 729 *Mercury*. Wiley, Hoboken, pp. 193-218.
- 730 Wang, K., Liu, G.L., Cai, Y., Possible pathways for mercury methylation in oxic marine waters.
- 731 *Critical Reviews in Environmental Science and Technology*.
- 732 Wang, W., Wong, R.S.K., Wang, J., Yen, Y., 2004. Influences of different selenium species on
- 733 the uptake and assimilation of Hg(II) and methylmercury by diatoms and green mussels.
- 734 *Aquatic Toxicology* 68, 39-50.
- 735 Wang, Y., Li, Y., Liu, G., Wang, D., Jiang, G., Cai, Y., 2015. Elemental Mercury in Natural
- 736 Waters: Occurrence and Determination of Particulate Hg(0). *Environmental Science &*
- 737 *Technology* 49, 9742-9749.
- 738 Wang, Y., Liu, J., Liem-Nguyen, V., Tian, S., Zhang, S., Wang, D., Jiang, T., 2022. Binding
- 739 strength of mercury (II) to different dissolved organic matter: The roles of DOM properties
- 740 and sources. *Science of The Total Environment* 807, 150979.
- 741 Weber, J.H., 1993. Review of possible paths for abiotic methylation of mercury(II) in the aquatic
- 742 environment. *Chemosphere* 26, 2063-2077.
- 743 Whalin, L., Kim, E.H., Mason, R., 2007. Factors influencing the oxidation, reduction, methylation
- 744 and demethylation of mercury species in coastal waters. *Marine Chemistry* 107, 278-294.
- 745 Wilkinson, K.J., Joz-Roland, A., Buffle, J., 1997. Different roles of pedogenic fulvic acids and
- 746 aquagenic biopolymers on colloid aggregation and stability in freshwaters. *Limnology and*
- 747 *Oceanography* 42, 1714-1724.
- 748 Wilkinson, S.C., Goulding, K.H., Robinson, P.K., 1989. Mercury accumulation and volatilization
- 749 in immobilized algal cell systems. *Biotechnology Letters* 11, 861-864.
- 750 Wu, P., Kainz, M.J., Bravo, A.G., Åkerblom, S., Sonesten, L., Bishop, K., 2019. The importance
- 751 of bioconcentration into the pelagic food web base for methylmercury biomagnification: A
- 752 meta-analysis. *Science of The Total Environment* 646, 357-367.
- 753 Wu, Y., Wang, W.-X., 2012. Thiol compounds induction kinetics in marine phytoplankton during
- 754 and after mercury exposure. *Journal of Hazardous Materials* 217-218, 271-278.
- 755 Wu, Y., Wang, W.-X., 2013. Differential acclimation of a marine diatom to inorganic mercury
- 756 and methylmercury exposure. *Aquatic Toxicology* 138-139, 52-59.
- 757 Wu, Y., Wang, W.-X., 2014. Intracellular speciation and transformation of inorganic mercury in
- 758 marine phytoplankton. *Aquatic Toxicology* 148, 122-129.
- 759 Wu, Z.Y., Li, Z.K., Shao, B., Zhang, Y.Y., He, W., Lu, Y.R., Gusvitskii, K., Zhao, Y.X., Liu,
- 760 Y.R., Wang, X.J., Tong, Y.D., 2022. Impact of dissolved organic matter and environmental
- 761 factors on methylmercury concentrations across aquatic ecosystems inferred from a global
- 762 dataset. *Chemosphere* 294.
- 763 Xing, Z., Zhao, T., Bai, W., Yang, X., Liu, S., Zhang, L., 2018. Temporal and spatial variation in
- 764 the mechanisms used by microorganisms to form methylmercury in the water column of
- 765 Changshou Lake. *Ecotoxicol Environ Saf* 160, 32-41.



- 766 Yang, L., Zhang, Y., Wang, F., Luo, Z., Guo, S., Strähle, U., 2020. Toxicity of mercury: Molecular  
767 evidence. *Chemosphere* 245, 125586.
- 768 Yin, X., Wang, L., Liang, X., Zhang, L., Zhao, J., Gu, B., 2022. Contrary effects of phytoplankton  
769 *Chlorella vulgaris* and its exudates on mercury methylation by iron- and sulfate-reducing  
770 bacteria. *Journal of Hazardous Materials* 433, 128835.
- 771 Zhang, D.Y., Lee, D.J., Pan, X.L., 2013. Desorption of Hg(II) and Sb(V) on extracellular  
772 polymeric substances: Effects of pH, EDTA, Ca(II) and temperature shocks. *Bioresource  
773 Technology* 128, 711-715.
- 774 Zhang, T., Hsu-Kim, H., 2010. Photolytic degradation of methylmercury enhanced by binding to  
775 natural organic ligands. *Nature Geoscience* 3, 473-476.
- 776 Zhang, X., Li, Y., Feng, G., Tai, C., Yin, Y., Cai, Y., Liu, J., 2018. Probing the DOM-mediated  
777 photodegradation of methylmercury by using organic ligands with different molecular  
778 structures as the DOM model. *Water Research* 138, 264-271.
- 779 Zhang, Y., Soerensen, A.L., Schartup, A.T., Sunderland, E.M., 2020. A Global Model for  
780 Methylmercury Formation and Uptake at the Base of Marine Food Webs. *Global  
781 Biogeochemical Cycles* 34, e2019GB006348.
- 782 Zhao, Q., Wang, J., OuYang, S., Chen, L., Liu, M., Li, Y., Jiang, F., 2021. The exacerbation of  
783 mercury methylation by *Geobacter sulfurreducens* PCA in a freshwater algae-bacteria  
784 symbiotic system throughout the lifetime of algae. *J Hazard Mater* 415, 125691.
- 785