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## Role of phytoplankton in aquatic mercury speciation and transformations

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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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24

25

Not Distribute



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.



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. 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.



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.



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. 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

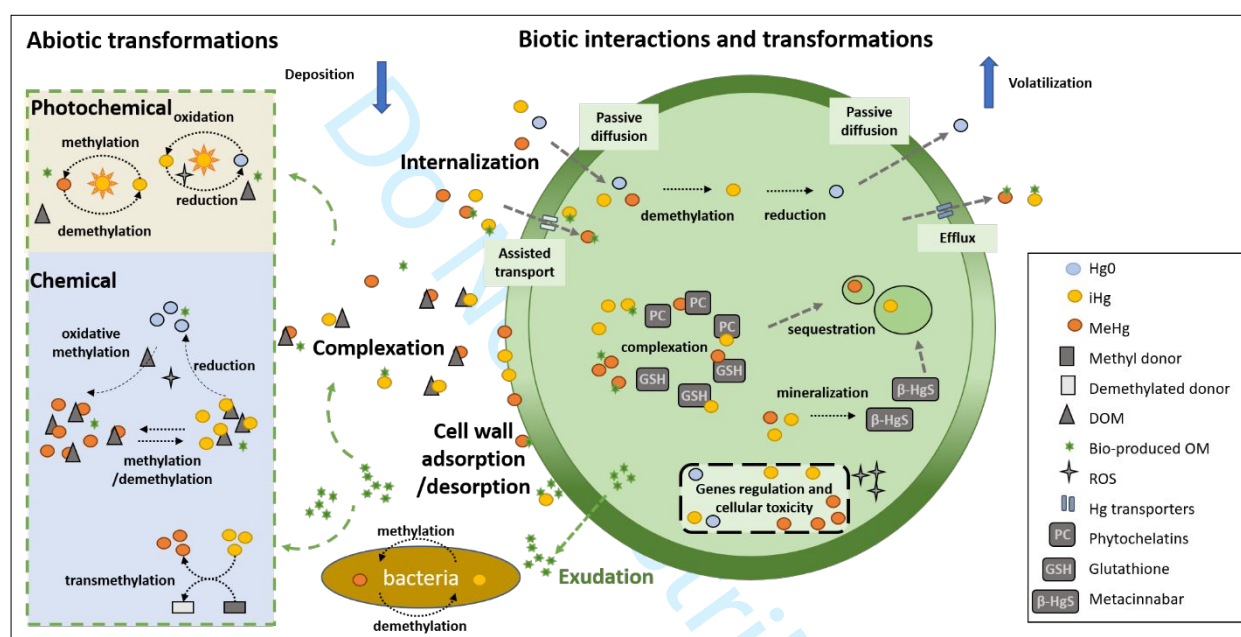
## 51 1. Introduction

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 (Lehnerr 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  $\text{Hg}^0$ , 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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