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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.



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 Hg⁰,
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

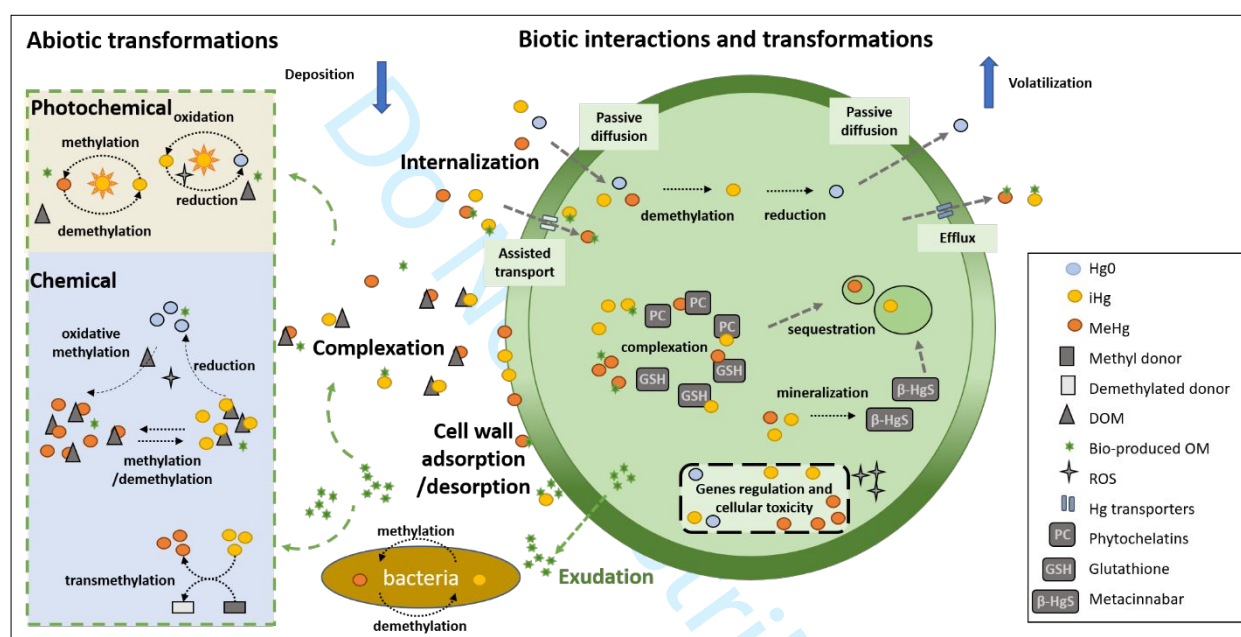
50

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 (Hg^0) and the methylation/demethylation of
60 iHg/monomethylmercury (MeHg, CH_3Hg). 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 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 Hg⁰ 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⁻¹) (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 Hg⁰ and Hg⁰ 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 Hg⁰ 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 H₂S 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 ¹O₂) (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 β -HgS.

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

238 The reduction of iHg to gaseous Hg⁰ 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 Hg⁰ 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 β -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 Hg⁰ (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 Hg⁰ 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). Hg⁰ 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 Hg⁰ (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 PC₂₋₃ 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 β -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 (β -HgS)
336 (Wu and Wang, 2014). The sunlight was also shown to facilitate the transformation of Hg to less
337 bioavailable species, such as β -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^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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