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Influence of oxygen, UV light and reactive dissolved organic matter on the photodemethylation and photoreduction of monomethylmercury

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Abstract — The key factors which affect the abiotic photodemethylation process of monomethylmercury (MMHg) in the freshwaters has remained unclear. Hence, this work aimed to better elucidate the abiotic photodemethylation pathway in a model freshwater. Anoxic and oxic conditions were implemented to investigate the simultaneous photodemethylation to Hg(II) and photoreduction to Hg(0). MMHg freshwater solution was irradiated through exposure to three wavelength ranges of full light (280-800 nm), without short UVB (305-800 nm), and visible light (400-800 nm). The kinetic experiments were performed following dissolved and gaseous Hg species concentrations (i.e., MMHg, iHg(II), Hg(0)). A comparison between two methods of post-irradiation purging and continuous irradiation purging confirmed MMHg photodecomposition to Hg(0) is mainly induced by a first photodemethylation step to iHg(II) followed by a photoreduction step to Hg(0). Photodemethylation under full light extent normalized to absorbed radiation energy showed a higher rate constant in anoxic conditions at $18.0 \pm 2.2 \text{ kJ}^{-1}$ compared to oxic conditions at $4.5 \pm 0.4 \text{ kJ}^{-1}$. Moreover, photoreduction also increased up to four-fold under anoxic conditions. Normalized and wavelength-specific photodemethylation (K_{pd}) and photoreduction (K_{pr}) rate constants were also calculated for natural sunlight conditions to evaluate the role of each wavelength range. The relative ratio in wavelength-specific K_{pd} PAR: $K_{pd \text{ long UVB+ UVA}}$: $K_{pd \text{ short UVB}}$ at 1: 74: 999, and 1:182:977 for anoxic and oxic conditions, respectively, demonstrate that the relative ratio is independent of the O₂ level, meaning O₂ is a simple inhibitor for photodemethylation process. The comparison

33 between the relative ratios for K_{pd} and K_{pr} showed higher dependence on UV light for photo-
34 reduction at least ten-fold compared to photodemethylation, regardless of redox conditions.
35 Both results using Reactive Oxygen Species (ROS) scavenging methods and Volatile Organic
36 Compounds (VOC) measurements revealed the occurrence and production of low molecular
37 weight (LMW) organic compounds that are as photoreactive intermediates responsible for
38 MMHg photodemethylation and iHg(II) photoreduction in the dominant pathway. This study
39 also supports the role of dissolved oxygen as an inhibitor for the photodemethylation path-
40 ways driven by LMW photosensitizers.

41 **Keywords**

42 *Photoreduction, Photodemethylation, Irradiation, Mercury speciation, gaseous mercury, redox*
43 *condition, Reactive oxygen species, Volatile organic compound, Reactive organic species*

1. INTRODUCTION

44

45 Monomethylmercury (MMHg) is a neurotoxin that accumulates in the food chain and
46 poses a health risk to humans. MMHg concentration remains low in surface waters due to its
47 photodemethylation into iHg and/or photoreduction to Hg(0) by sunlight. Photodemethyla-
48 tion and photoreduction are therefore among the major processes that maintain MMHg con-
49 centration at a low level and limit its uptake by biota in aquatic systems (*Amyot et al., 1994*;
50 *Seller et al., 1996*).

51 In previous works, UVB, UVA, and visible light contribution to MMHg photodemethyla-
52 tion (*Black et al., 2012; Fernández-Gómez et al., 2013; Kim et al., 2017*) and iHg photoreduc-
53 tion (*Garcia et al., 2005; O'Driscoll et al., 2018*) was determined. *Duval et al., (2023)* reported
54 important photoreduction in the Pyrenean lakes under important solar radiation and oligo-
55 trophic condition (DOC < 385 $\mu\text{mol L}^{-1}$). Although a recent work showed higher MMHg photo-
56 decomposition rate for 2- 10 times in eutrophic (DOC from 508 to 825 $\mu\text{mol L}^{-1}$) lake waters in
57 comparison with mesotrophic (DOC < 375 $\mu\text{mol L}^{-1}$) waters (*Bouchet et al., 2022*), *Garcia et*
58 *al., (2005)* has reported higher yield for Hg(0) production in clear lake waters under UVB irra-
59 diation. Similar results were obtained in the comparison of photoreduction rate between the
60 river and lake waters (*O'Driscoll et al., 2018*). They observed that the photoreduction rate
61 constant in DOM-rich lake waters was significantly lower than that in DOM-poor river samples
62 under UVB irradiation, whereas these constants did not differ in lake and river waters under
63 UVA irradiation. This negative correlation between Hg(0) production and DOM concentration
64 is related to either the light absorption by DOM which limits its transmission in waters in the
65 order of visible light > UVA > UVB (*Black et al., 2012; Kim et al., 2017; Watras et al., 1995; Zhang*
66 *et al., 2017*) or Reactive Oxygen Species (ROS) quenching by high DOM concentration
67 (*Fernández-Gómez et al., 2013*). As well, *Black et al., (2012)* reported a decrease in MMHg
68 photodecomposition up to 6% by increasing DOM concentration from 83 to 917 $\mu\text{mol L}^{-1}$ of
69 DOC.

70 The solar irradiation affects the characteristics of DOM which lead to changes in its com-
71 position and influence its role in the Hg cycle. For instance, the aromatic and quinoid struc-
72 tures mainly in terrestrial DOM act as strong photosensitizers that can absorb the available
73 wavelength (hydroquinone absorbance at 288 nm, *Sirajuddin et al., 2007*) and promote MMHg
74 photodemethylation pathways (*Fleck et al., 2014; Qian et al., 2014; Zhang et al., 2017*).

75 *Fantozzi et al., (2007)* pointed out that some chromophoric group in DOM plays an important
76 role in Hg(0) production owing to the complexation of iHg to the carboxyl groups in organic
77 matter and, thereby promoting the light-induced production of Hg(0). Another work showed
78 that the photoreduction rate is affected not only by the functional groups such as -OH and -
79 COOH on the aromatic cycles but also by the position of these functional groups on the ring
80 structure (*He et al., 2012*). A strong correlation between UV absorption of DOM molecules
81 and DOM concentrations led to suggest that iHg photoreduction results from the DOM pho-
82 tolysis and the subsequent formation of high ROS production and intramolecular electron
83 transfer via Hg complexation to photoreactive DOM (*Han et al., 2017; He et al., 2012; Tai et*
84 *al., 2014; Whalin et al., 2007*). MMHg photodemethylation rate is influenced by competition
85 between complexation reagents to MMHg (*Tai et al., 2014*). For instance, reduced DOM (low
86 oxidation state) participates in photodemethylation 3 times faster than oxidized DOM (*Qian*
87 *et al., 2014*). These authors indicated that MMHg photodemethylation process requires a syn-
88 ergic effect between strong binding MMHg- ligand i.e., thiol (*Chandan et al., 2015*) and direct
89 energy transfer from photoreactive moieties such as aromatic cycles to break the Hg-C bonds
90 (*Qian et al., 2014*). In addition, water components such as chloride (Cl⁻), nitrate (NO₃⁻), and
91 iron (Fe(III)) are important factors in affecting substantially the photodemethylation rate (*Sun*
92 *et al., 2017*).

93 Under oxic conditions, various studies have given different conclusion about ROS in-
94 volved in MMHg photochemical reactions that are summarized here: i) hydroxyl radicals (*OH)
95 produced through photo-Fenton reactions (*Kim and Zoh, 2013*) or NO₃⁻ photolysis (*Chen et al.,*
96 *2003; Kim and Zoh, 2013*), and its production can be enhanced by pH increase in freshwaters
97 (*Kim et al., 2017; Kim and Zoh, 2013*) and ii) Singlet oxygen (¹O₂) which has been shown as a
98 highly reactive photodemethylation driver (*Zhang and Hsu-Kim, 2010*). The suggested MMHg
99 photochemical pathways can be summarized as i) direct photodissociation of the C-Hg bond
100 (*Han et al., 2017; Inoko, 1981; Tai et al., 2014*); ii) indirect pathways involving ROS and free
101 radicals induced by DOM photolysis reactions (*Chen et al., 2003; Hammerschmidt and*
102 *Fitzgerald, 2010; Zhang, 2006; Zhang and Hsu-Kim, 2010*). Unlike the previous cited work, a
103 study showed that the addition of various *OH, and ¹O₂ scavengers did not result in a MMHg
104 photodemethylation decrease (*Black et al., 2012*). These authors concluded that MMHg pho-
105 todemethylation can occur via various pathways; and iii) direct photolysis via intramolecular

106 charge transfer within the MMHg-DOM complexes (*He et al., 2012; Tai et al., 2014; Whalin et*
107 *al., 2007*).

108 Therefore, because of a lack of consensus and comprehension of the underlying mech-
109 anisms and environmental effects on MMHg photochemical reactions, our current work aims
110 to investigate and further determine the dominant pathway of this process. As MMHg pho-
111 todemethylation has been considered a one-step process to produce either Hg(0) as the main
112 product (*Chen et al., 2003; Li and Cai, 2013; Zhang et al., 2018*) or only iHg (*Gårdfeldt et al.,*
113 *2001*), three Hg species including MMHg, iHg, and Hg(0) were measured throughout our study
114 to evaluate MMHg photodemethylation to iHg as the first step of this reaction. To assess how
115 the environmental condition affects mechanistic pathways of the MMHg photochemical pro-
116 cess, and its fate in freshwaters, this study investigated three major factors including (i) differ-
117 ent regions of the solar spectrum full light (280-800 nm), without short UVB (305-800 nm),
118 and visible light (400-800 nm); (ii) two different redox conditions to evaluate the UV light role
119 in ROS production, and (iii) two purging modes (post-irradiation and continuous irradiation)
120 to determine the role of gaseous Hg(0) in re-oxidation reaction.

121 2. MATERIAL AND METHODS

122 Experimental design

123 The experiment was performed in 50 mL PFA containers by mixing 35 mL of SRFA so-
124 lution at 560 mmolL⁻¹ of DOC with MMHg solution at 0.25 μmolL⁻¹ to obtain a DOC/Hg
125 (mol./mol.) ratio at 2000 to ensure that DOM ligands are in excess (*Zheng and Hintelmann,*
126 *2010*). The initial pH of solution was adjusted to pH 6.5-7 using ultrapure HCl and NaOH. This
127 range of pH corresponds to typical pH in surface waters (e.g. *Ilina et al., 2013*). Reactors were
128 wrapped in aluminum foil and stirred overnight in a dark room to equilibrate MMHg complex-
129 ation with DOM. For the first purging-mode, post-irradiation purging (Post-ip) experiment: i)
130 wrapped reactors were then purged with argon (Ar), and/ or pure air (previously cleaned by
131 set-up a gold trap) for 10 min with a gas flow at 100 mL min⁻¹ to produce anoxic and oxic
132 conditions, respectively (*Fig.S1a*), ii) solutions were then irradiated for 3, 10, 30, and 60 min
133 (*Fig.S1b*), and iii) solutions were again purged by Ar for 10 min at 100 mL min⁻¹ to collect Hg(0)
134 on a trap (*Fig.S1c*). For the second purging-mode, continuous irradiation purging (Cont-ip) ex-
135 periment, solutions were continuously purged during the irradiation using Ar and/ or pure air

136 (Fig.S1d) with adequate gas flow, calculated according to irradiation time to obtain > 99%
137 purging efficiency of Hg(0) (Gärdfeldt et al., 2002). The Hg(0) was collected through trapes
138 made of a quartz glass tube filled with gold-coated silica (Amasil™ with a trapping capacity of
139 82 mg of Hg, a recovery > 97% at 30°C <T < 210°C), were purchased from P S Analytical. The
140 remained solutions were acidified at 1% HCl (v/v) and stored in dark at 4°C to analyze MMHg
141 and iHg concentrations. The solutions were irradiated using a polychromatic light source (Oriel
142 Instruments with a 300 W Xe arc lamp) with a beam turning Mirror, full reflector, (Newport
143 66215). Temperature was controlled by extracting heat under a fume hood. To avoid the un-
144 controllable emission of light from surfaces, light emission to solutions was directed through
145 a cutout window on an aluminum sheet. The distance between the solutions and the light
146 source was 20.5 cm (Fig.S2). Experiment was carried out under three wavelength ranges full
147 light (280- 800 nm, irradiance ($I_{\text{simulator}}$) at 29 mW cm⁻²), no short UVB (305- 800 nm, $I_{\text{simulator}}=$
148 27 mWcm⁻²) using a 65CGA-305 filter (GB328) and Photosynthetically Active Radiation (PAR =
149 400- 800 nm, $I_{\text{simulator}}= 12 \text{ mWcm}^{-2}$) using a 65CGA-400 filter (CA222). Irradiances of simulator
150 and natural sunlight are reported in Supplementary Information. These data illustrate the
151 choice to use the high intensity of simulator irradiance under short UVB wavelength range
152 (280-305 nm) compared to that for natural sunlight (I_{sunlight}), $I_{\text{simulator}}: I_{\text{sunlight}}$ at 38:1 (Fig.S3).

153 All the experiments were performed in triplicate, and experimental uncertainty was
154 calculated by standard deviations (SD) of triplicate samples. Two series of control experiments
155 were performed under dark (wrapped reactors using aluminum foil) and without DOM, under
156 the same conditions as described above. Under oxic conditions, role of ROS in the photode-
157 methylation pathways was determined using three scavengers including isopropanol, iso-
158 prene, and sodium azide (NaN₃) as probes of •OH, triplet excited state dissolved natural or-
159 ganic matter (³NOM*), and ¹O₂, respectively (Buxton et al., 1988; Boreen et al., 2008; Miyoshi
160 et al., 1982). To test the reactivity of these scavengers to photoreactive intermediates species
161 including ROS and reactive organic species, scavenger experiment was investigated under an-
162 oxic condition, whereby almost no O₂-drived ROS can be produced. In addition, iron chloride
163 (FeCl₃) was used as a hydroquinone scavenger (Jiang et al., 2015) under two redox conditions.
164 All steps of Hg species analyses, DOM characterization, ROS measurement, scavenger experi-
165 ment, and calculation of photodemethylation and photoreduction rate constants are de-
166 scribed in details in the Supplementary Information file.

167

3. RESULTS

3.1 Effect of redox condition on MMHg photodemethylation

169 In this work, the photodemethylation term is employed for the photochemical trans-
170 formation of MMHg into iHg while photoreduction indicates the iHg photochemical reduction
171 process to Hg(0). Three Hg species yields, MMHg%, iHg%, and gaseous Hg(0)% were normal-
172 ized according to the total MMHg initially added into the solutions. The irradiation times (s)
173 were converted to absorbed energy (J) using measured simulator irradiance (W cm^{-2}) and reac-
174 tor's physical parameters (Supplementary Information, Section 3). No evidence of abiotic de-
175 methylation or reduction was observed in dark control experiment (Table S1). In post-irradi-
176 ation purging (Post-ip) experiment, under full light with absorbed energy at 4J, MMHg was pho-
177 todemethylated to $2\pm 1\%$ iHg, and $4\pm 2\%$ was photoreduced to Hg(0) under anoxic conditions
178 whereas, under oxic conditions, MMHg was photodemethylated to $1\pm 1\%$ iHg and photore-
179 duced to $1\pm 0\%$ Hg(0) (Fig.1a, Fig.S4a and Table S2). With absorbed energy increasing to 206J,
180 iHg and Hg(0) proportions rose to $8\pm 2\%$ and $23\pm 6\%$, respectively, under anoxic conditions.
181 Whereas, under the oxic condition, $9\pm 1\%$ iHg and $6\pm 0\%$ Hg(0) were produced (Fig.1a, Fig.S4a
182 and Table S2).

183 Without short UVB at 3J absorbed energy, under anoxic conditions, MMHg was pho-
184 todemethylated and photoreduced to $4\pm 1\%$ iHg and $2\pm 0\%$ Hg(0), respectively (Fig.1b, Fig.S4b
185 and Table S2). With energy increasing to 185J, iHg and Hg(0) proportions increased to $8\pm 2\%$
186 and $17\pm 1\%$, respectively. Under oxic conditions, similar results to the full light condition were
187 observed regardless of the lower absorbed energy.

188 No Hg(0) was produced in anoxic and oxic conditions, under PAR light. However, under
189 anoxic conditions, photodemethylation occurred through slight iHg production from up to
190 $6\pm 3\%$ by increasing energy from 3J to 31J (Fig.1c, Fig.S4c and Table S2) whereas, under oxic
191 conditions, no significant variation was observed in iHg production, despite higher absorbed
192 energy at 61J.

193 Our calculated data showed higher values for photodemethylation (k_{pd}) and photore-
194 duction (k_{pr}) rate constants under anoxic compared to oxic conditions independent on light
195 wavelength ranges (Table S3). Under full light, the k_{pd} and k_{pr} were calculated at 18.00 ± 2.19
196 kJ^{-1} , and $11.10\pm 0.49 \text{kJ}^{-1}$ for anoxic conditions, four-folds higher than those under oxic condi-

197 tions at $4.52 \pm 0.39 \text{ kJ}^{-1}$, and $2.78 \pm 0.20 \text{ kJ}^{-1}$, respectively (Table S3). Similar results were ob-
198 served for k_{pd} and k_{pr} , meaning higher values in anoxic conditions up to three-fold compared
199 to oxic conditions. After a correction of natural sunlight irradiance at specific wavelengths Eq.
200 8 to Eq.10 (Supplementary Information), wavelength-specific $K_{pd \text{ PAR}}$, $K_{pd \text{ long UVB+ UVA}}$, and K_{pd}
201 short UVB were determined at 0.4 ± 0.1 , 26.1 ± 2.5 , and $357.4 \pm 84.5 \text{ kJ}^{-1}$ for anoxic condition, and
202 0.1 ± 0.1 , 10.0 ± 1.0 , and $55.3 \pm 17.3 \text{ kJ}^{-1}$ for oxic conditions, respectively (Table 1). Moreover, K_{pr}
203 results presented negligible values for photoreduction under PAR regardless redox conditions.
204 Under natural sunlight, a general trend can be outlined: i) under similar conditions, $K_{pd} > 1.4$
205 K_{pr} , ii) photodemethylation showed higher rates under short UVB than those under long UVB+
206 UVA for fourteen- and six-folds in anoxic and oxic conditions, respectively, iii) photoreduction
207 also presented higher rates under short UVB than those under long UVB+ UVA for thirteen-
208 and five-folds in anoxic and oxic conditions, respectively, and iv) in similar irradiation condi-
209 tions:, K_{pd} and K_{pr} showed higher rates in anoxic condition than those in oxic condition for six-
210 and three-folds under short UVB, and long UVB+UVA, respectively (Table 1).

211 3.2 Effect of purging mode on MMHg photodemethylation

212 In the continuous irradiation purging (Cont-ip) experiment, under full light and anoxic
213 conditions, 8% of MMHg was photodemethylated to $5 \pm 2\%$ iHg and photoreduced $3 \pm 1\%$ Hg(0)
214 at 34J of energy (Fig.1d, Fig.S4d and Table S4). Similar to the Post-ip experiment (section 3.1),
215 iHg and Hg(0) proportions increased to $8 \pm 2\%$ and $16 \pm 5\%$, respectively with energy increasing
216 to 205 J. Under oxic conditions, with uncertainty consideration, iHg and Hg(0) varied within
217 the same range as the Post-ip experiment results, from $3 \pm 1\%$ to $9 \pm 2\%$ and from $2 \pm 0\%$ to $8 \pm 2\%$,
218 respectively whereby energy was increased from 34J to 206J.

219 Under anoxic conditions, without short UVB with energy at 31J, MMHg was photode-
220 methylated to $3 \pm 3\%$ iHg and photoreduced to $2 \pm 0\%$ Hg(0) (Fig.1e, Fig.S4e and Table S4). These
221 Hg species proportions increased to $5 \pm 1\%$ and $7 \pm 1\%$, respectively by increasing energy to 185J.
222 Under oxic conditions, similar results to the Post-ip experiment (section 3.1) were again ob-
223 tained meaning iHg and Hg(0) rose from $2 \pm 0\%$ to $3 \pm 0\%$ and from $1 \pm 0\%$ to $5 \pm 0\%$, respectively,
224 by energy increase from 8J to 192J.

225 No Hg(0) production was observed under PAR light, regardless of the redox condition
226 (Fig.1f, Fig.S4f and Table S4). Under anoxic conditions by energy increasing from 10J to 31J,
227 MMHg photodemethylation improved slightly from $1 \pm 0\%$ to $7 \pm 1\%$ for iHg, whereas, under

228 oxic conditions, it presented insignificant variation, despite a higher variation in absorbed en-
229 ergy from 5J to 61J.

230 **3.3 Chemical characterization of dissolved organic matter and light absorption**

231 The Post-ip experiment showed insignificant MMHg photodemethylation and photo-
232 reduction without DOM under two redox conditions (Table S5). The solutions were character-
233 ized through i) cations, anions, and dissolved organic carbon concentration analyses (Tables
234 S6 and S7), ii) measurement of UV-Visible spectra (280-800 nm) of remained solutions (Fig.S5),
235 and iii) measurement of Volatile Organic Compounds (VOC with mass/ charge < 300) produced
236 in pre-and post-irradiation solutions under anoxic and oxic conditions. Insignificant variation
237 was observed in chemical elements concentrations regarding redox conditions (Table S6). The
238 pH and Eh were measured at 6.3 and 230 mV in the initial solution, respectively. Under anoxic
239 conditions, pH increased to 7.5 and Eh decreased to 90 mV in pre-irradiation solution. The pH
240 decreased to 7.0 and Eh reached 130 mV in post-irradiation step at 39 J of absorbed energy.
241 Under oxic conditions, in pre-, and post-irradiation steps, pH and Eh varied within a small
242 range from 6.0 to 6.3 and from 210 mV to 230 mV, respectively. The UV-Visible spectra of
243 remained solutions were measured from 280 nm to 800 nm (Fig.S5). Lower absorbances were
244 observed in oxic conditions. From this dataset, the Specific UV Absorbance (SUVA) value was
245 calculated at 254 nm wavelength representing the aromaticity and humification index of the
246 DOM (Fig.S6, and Table S8). For a specific adsorbed energy, SUVA values confirmed the latter
247 results meaning $SUVA_{\text{Anoxic-No short UVB}} > SUVA_{\text{Anoxic-Full light}} > SUVA_{\text{Oxic-No short UVB}} > SUVA_{\text{Oxic-Full light}}$
248 for both Post-ip and Cont-ip experiments (Fig.S6). The SIFT-MS analyses in pre-irradiation sam-
249 ples showed two matrices with VOCs content under anoxic and oxic conditions (Fig.S7). The
250 presence of five identical VOCs was confirmed in the pre-irradiation steps under anoxic and
251 oxic conditions (Table S9). These VOCs presented mass to charge ratio (m/z) at 57, 73, and 211
252 for precursor O_2^+ , and 62, and 130 for precursor OH^- . In the post-irradiation step, the SIFT-MS
253 analyses revealed production of various VOCs under anoxic and oxic conditions (Fig.S8). The
254 m/z ratios and intensities of these VOCs were listed in Table S10. SIFT-MS analyses showed
255 production of phenolate with m/z ratio at 93 for precursor O_2^- in pre-and post-irradiation sam-
256 ples under anoxic conditions. Moreover, the appearance of propanal and acetaldehyde was
257 detected in the pre-and post-irradiation steps under both redox conditions (Table S10).

258 3.4 Measurement of potential production of reactive oxygen species

259 Results of the ROS analyses showed a higher potential production of HTA as probe of
260 $\cdot\text{OH}$, under anoxic conditions than oxic conditions (Fig.S9a). $\cdot\text{OH}$ production increased four-
261 fold under anoxic compared to oxic conditions. A similar result was obtained for XTT absorb-
262 ance measurement indicating four-fold higher potential production of superoxide radical ($\text{O}_2^{\cdot-}$
263) under anoxic compared to oxic conditions (Fig.S9b, and Table S11). Under oxic conditions,
264 insignificant variations were observed for the iHg and Hg(0) production in the presence of
265 isoprene, and isopropanol compared to the experiment without scavenger (Table S12 and
266 Fig.S10). Addition of sodium azide slightly inhibited MMHg photodegradation for 7% and led
267 to production of $2\pm 1\%$ iHg and $6\pm 1\%$ Hg(0). Although, sodium azide is well-known as $^1\text{O}_2$ under
268 oxic conditions, it surprisingly inhibited photodemethylation and photoreduction by the pro-
269 duction of $7\pm 1\%$ iHg and $1\pm 0\%$ Hg(0), under anoxic conditions. Under anoxic conditions, the
270 addition of isoprene and isopropanol scavengers showed insignificant results in MMHg pho-
271 todemethylation to iHg, and also photoreduction to Hg(0) compared to the experiment with-
272 out scavengers. Iron(III) addition promoted MMHg photodemethylation up to $40\pm 2\%$ iHg
273 whereas, it suppressed iHg photoreduction to Hg(0) at $18\pm 2\%$.

274 4. DISCUSSION

275 4.1 A two-step mechanism of photodemethylation and photoreduction

276 In agreement with our work, an enhancement in MMHg photodemethylation was pre-
277 viously observed under anoxic compared to oxic conditions (Pan et al., 2017). A simple com-
278 parison between the Post-ip and Cont-ip experiments data, under the same conditions i.e.,
279 redox and wavelength, revealed the production of the same proportion of iHg with uncertain-
280 ties consideration (Fig.1, and Tables S2 and S4). The most important outcome of this compar-
281 ison confirms our hypothesis that MMHg photodecomposition is mainly induced by the first
282 step of C-Hg bond cleavage meaning MMHg photodemethylation to iHg(II) and then followed
283 by iHg(II) photoreduction step to Hg(0). The second outcome of these results showed that this
284 process includes no back Hg(0) oxidation. Indeed, observation of higher Hg(0) production un-
285 der anoxic conditions in the Post-ip experiment whereby Hg(0) can be oxidized to iHg, sug-
286 gested that the iHg photoreduction step to Hg(0) is performed as an almost irreversible reac-
287 tion and Hg(0) oxidation is negligible. Using Box Lucas 2 exponential fitting model and kinetic

288 data supported this fact that MMHg photochemical process is as pseudo first-order which in-
289 cludes two first-order successive reactions (Supplementary Information, Section 3).

290 4.2 Oxygen influences on photodemethylation and photoreduction

291 ROS implication in photodemethylation and photoreduction processes has been de-
292 bated in several studies. On one side, some previous works presented ROS, including $\cdot\text{OH}$
293 (Chen et al., 2003; Hammerschmidt and Fitzgerald, 2010) and $^1\text{O}_2$ (Black et al., 2012; Kim et
294 al., 2017; Suda et al., 1993; Zhang and Hsu-Kim, 2010) as intermediate compounds responsible
295 for photodemethylation and photoreduction, on the other side, several works showed that
296 ROS has a minor role and MMHg photochemical reactions occur by intramolecular charge
297 transfer by DOM (Tai et al., 2014; Zhang et al., 2018). Nevertheless, Fernández-Gómez et al.,
298 (2013) explained that ROS production is related to DOM photolysis, therefore DOM controls
299 ROS production, and even an increase in DOM can quench ROS and limits MMHg photode-
300 methylation as shown by Kim and Zoh, (2013). DOM reactivities in two redox condition are
301 subject of the following discussion in section 4.4.

302 According to literature, $\cdot\text{OH}$ production can result from two processes: i) photolysis of
303 nitrogen-containing DOM (Vione et al., 2006; Warneck and Wurzinger, 1988), and ii) photo-
304 Fenton process enhancement because of DOM and Fe interactions (Voelker and Sulzberger,
305 1996). Although an experimental study has shown $\cdot\text{OH}$ production from the photolysis of NO_3^-
306 enables MMHg photodemethylation (Chen et al., 2003), another experimental study in surface
307 coastal waters has contradicted and reported that NO_3^- concentration does not control pho-
308 todemethylation (DiMento and Mason, 2017). However, average NO_3^- and Fe(III) concentra-
309 tions were measured herein in the solutions at $9 \mu\text{mol L}^{-1}$ and $0.2 \mu\text{mol L}^{-1}$, respectively (Table
310 S6), both lower than reported values (NO_3^- our work $< 620 \mu\text{mol L}^{-1}$ Chen et al., 2003, and Fe our
311 work $< 2 \mu\text{mol L}^{-1}$ Voelker and Sulzberger, 1996) which affected MMHg photodemethylation.
312 Our ROS measurements seem to indicate higher potential production of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ under
313 anoxic conditions (Fig.S9). It should be noted that $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ production requires O_2 occur-
314 rence which was negligible under anoxic conditions ($E_h=90\text{mV}$) and also ROS production is
315 expected to increase under oxic conditions and decrease under anoxic conditions (Kong and
316 Zepp, 2012; Xu et al., 2011). ROS that have been often recognized as a critical factor in MMHg
317 photodemethylation pathways (Black et al., 2012; Chen et al., 2003; Hammerschmidt and
318 Fitzgerald, 2010; Zhang, 2006; Zhang and Hsu-Kim, 2010), while they do not play an important

319 role in MMHg photodegradation under our conditions. In addition, these results raise the
320 question on the selectivity of XTT and HTA probes (*Šnyrychová & Hideg, 2008; Sutherland &*
321 *Learmonth, 1997*) for these two ROS species and their reactivities against other reactive or-
322 ganic species produced by DOM photolysis e.g., low molecular weight (LMW) carbonyl groups
323 of amino acids (*Bertilsson and Tranvik, 2000; Kieber and Blough, 1990; Kieber et al., 1990*).
324 Since insignificant differences in photodemethylation and photoreduction were also found
325 with and without isopropanol under oxic and anoxic conditions (*Table S12*), $\cdot\text{OH}$ role in MMHg
326 photodemethylation was downplayed. However, results showed remarkable inhibition of pho-
327 todemethylation and photoreduction by NaN_3 , suggesting that $^1\text{O}_2$ was partly responsible for
328 photodemethylation and photoreduction under anoxic and oxic conditions (*Table S12*). Alt-
329 hough NaN_3 was recognized as a $^1\text{O}_2$ scavenger in photocatalytic reactions (*Gao et al., 2019;*
330 *Kim et al., 2017; Nosaka and Nosaka, 2017; Zhang et al., 2017*), adding NaN_3 with a concen-
331 tration $> 100 \text{ mmol L}^{-1}$ showed a significant inhibition effect on the formation of MMHg-DOM
332 complexes up to 50% (*Han et al., 2017*). Furthermore, a previous study has proven that $^1\text{O}_2$
333 cannot be involved in MMHg photodemethylation as a primary driver (*Tai et al., 2014*). They
334 observed insignificant variation in MMHg photodemethylation rate by adding $\text{MoO}_4^{2-}/\text{H}_2\text{O}_2$,
335 as a $^1\text{O}_2$ generator. It is also worth to mention that a previous study has shown N_3^- as efficient
336 acceptors of carbon radicals (*Minozzi et al., 2009*). Either N_3^- suppresses MMHg-DOM com-
337 plexation, or it interacts with organic carbon radicals, inhibition of MMHg photochemical re-
338 actions by N_3^- under anoxic and oxic conditions cannot be consequently interpreted as an ef-
339 fect of $^1\text{O}_2$ on these reactions. This supports the hypothesis of the production of other types
340 of photosensitive intermediates such as reactive organic species (discussed in section 4.4) with
341 similar reactivities as ROS toward XTT, TA, and N_3^- . Therefore, based on our specific approach
342 comparing oxic and anoxic conditions, we can suggest that neither $\cdot\text{OH}$ nor $^1\text{O}_2$ play a role in
343 MMHg photodemethylation and iHg photoreduction reactions under such conditions.

344 In agreement with (*Tai et al., 2014; Zhang et al., 2018*), significantly higher k_{pd} and k_{pr}
345 were measured under full light compared to without short UVB, whatever redox conditions
346 (*Table S3*). Except in oxic condition for Cont-ip experiment which presented a similar k_{pd} and
347 k_{pr} under full light and without short UVB which varied within the same range with uncertain-
348 ties consideration. Our results indicate four-fold higher rates for both k_{pd} and k_{pr} under anoxic
349 compared to oxic conditions under full light in Post-ip experiment (*Table S3*). These results are
350 consistent with previous works which have reported the higher k_{pd} under anoxic conditions

351 up to three-fold (*Pan et al., 2017; Tai et al., 2014*). Our results therefore suggest that O₂ pres-
352 ence inhibits probably MMHg phototransformation processes. This finding confirm the exper-
353 imentally hypothesis suggesting that O₂ may serve as a scavenger of some intermediates spe-
354 cies for this process (*Tai et al., 2014*).

355 **4.3 Role of ultraviolet light on photodemethylation and photoreduction**

356 Normalized results of MMHg photochemical reactions rate constants under natural sun-
357 light confirmed higher K_{pd} and K_{pr} under short UVB (**Table 1**). Several studies have previously
358 determined the relative wavelength effects of UVB, UVA, and PAR on the MMHg photode-
359 methylation with a UV radiation contribution > 70% (*Black et al., 2012; DiMento and Mason,*
360 *2017; Fernández-Gómez et al., 2013*). Although UVA has been recognized as responsible for
361 photodemethylation in seawaters (*DiMento and Mason, 2017; Zhang and Hsu-Kim, 2010*), PAR
362 contribution dominates in turbid waters (estuarine and wetland) because of the more rapid
363 attenuation of UV light across the water column with high DOM concentration (*Black et al.,*
364 *2012*). However, our results showed slight photodemethylation (e.g. $K_{pd\ PAR} < 0.4\ \text{kJ}^{-1}$) and pho-
365 toreduction (e.g. $K_{pr\ PAR} < 20\ \text{J}^{-1}$) whatever redox conditions (**Table 1**), suggesting important
366 influence of UV light on photodemethylation and photoreduction reactions. The relative ratio
367 of $K_{pd\ PAR} : K_{pd\ long\ UVB+UVA} : K_{pd\ short\ UVB}$ was obtained at 1: 74: 999, and 1:182:977 for anoxic and
368 oxic conditions under natural sunlight, respectively. These high relative ratios under oxic com-
369 pared to those under anoxic conditions are related to the lowest $K_{pd\ PAR}$ at $0.1\ \text{kJ}^{-1}$ under oxic
370 conditions. Similar ratios have been reported at 1:43:3100, and 1:37:400 for $K_{pd\ PAR} : K_{pd\ UVA} : K_{pd}$
371 $_{UVB}$ in lake-wetland waters, under oxic conditions (*Black et al., 2012; Fernández-Gómez et al.,*
372 *2013*). The disagreement can be referred to variation in wavelength ranges, light irradiance,
373 DOM composition, and O₂ concentration in waters. A different result of the relative ratio of
374 $K_{pr\ PAR} : K_{pr\ long\ UVB+UVA} : K_{pr\ short\ UVB}$ at 1:853:10887, and 1:1810:9651 was obtained for anoxic and
375 oxic conditions under natural sunlight, respectively (**Table 1**). These high relative ratios are
376 related to the negligible normalized values of $K_{pr\ PAR}$ at 20 and $4\ \text{J}^{-1}$ in anoxic and oxic conditions
377 under natural sunlight, respectively. These latter relative ratios showed a major role of UV
378 light in the order: short UVB > long UVB+UVA in the photoreduction reaction, regardless redox
379 conditions.

380 4.4 Low molecular weight organic compound as reactive drivers for MMHg photochemical 381 processes

382 The main factor influencing DOM photoreactivity between two redox conditions might
383 result from the production of various reactive organic compounds. In post-irradiation step, a
384 comparison of VOC measurement results revealed production of different VOCs with
385 mass/charge < 300 through DOM photolysis in oxic and anoxic conditions (Table S10). These
386 results are consistent with previous works that have shown higher photodemethylation rate
387 in the presence of LMW organic matter, i.e. < 3.5 kDa due to the high photosensitization effi-
388 ciency (Kim *et al.*, 2017; Tai *et al.*, 2014; Zhang *et al.*, 2017). Production of phenolate as one
389 of the VOCs which was detected only in anoxic conditions confirmed difference in DOM reac-
390 tivity following photolysis under various redox conditions. These results suggested the contri-
391 bution of phenolate (and similar derivatives) as a reactive chromophore in photodemethyla-
392 tion and photoreduction in anoxic conditions. According to pK_a of phenol at 7.2 (Zhu *et al.*,
393 2000), during anoxic condition when pH of the solution goes beyond its pK_a i.e. 7.5, phenols
394 exists as negative phenolate which was detected by VOC measurement. SRFA contains abun-
395 dant LMW functional groups, such as phenols (Zhang *et al.*, 2018, Table S13) or hydroquinone
396 (Zheng *et al.*, 2012; Fleck *et al.*, 2014; Ratasuk and Nanny, 2007) which can participate in iHg
397 photoreduction via intramolecular electron through UV-light absorption (at 288 nm,
398 Sirajuddin *et al.*, 2007) and photoexcitation (Zheng *et al.*, 2012). Under oxic conditions, phenol
399 was hydroxylated in para positions, yielding hydroquinone (Andrade *et al.*, 2006; Quintanilla
400 *et al.*, 2006; Santos *et al.*, 2002) which was immediately oxidized to quinone in the presence
401 of O₂ (Lerner *et al.*, 2006), whereas under anoxic conditions, phenol hydroxylation and hydro-
402 quinone oxidation were prevented due to lack of •OH and O₂. In our work, adding Fe(III) as
403 hydroquinone scavenger proved their role in iHg photoreduction (Fig.S10 and Table S12). Un-
404 der oxic conditions, Fe inhibits iHg photoreduction by scavenging hydroquinone moieties and
405 its oxidation to quinone (Jiang *et al.*, 2015) and finally suppresses its participation in photore-
406 duction, whereas under anoxic conditions, oxidation of hydroquinone by Fe was prevented
407 because of the lack of O₂. These data highlighted phenol and hydroquinone roles in iHg pho-
408 toreduction reaction in anoxic conditions. The importance of LMW organic compounds for
409 MMHg photodemethylation and photoreductions processes was revealed through a compar-

410 ison between the Post-ip and the Cont-ip experiments, meaning higher k_{pd} and k_{pr} were ob-
411 tained for the Post-ip experiment under the same experimental condition (Table S3). Indeed,
412 the lower k_{pd} and k_{pr} were obtained for the Cont-ip experiment when VOCs were removed
413 from the solutions with continuous purging. These results support that these LMW organic
414 compounds promote MMHg photodemethylation and iHg photoreduction reactions.

415 In a previous work, *Pan et al., (2017)* explained a high photodemethylation rate ob-
416 served under anoxic conditions through $^3\text{NOM}^*$ scavenging by O_2 under oxic condition. How-
417 ever, insignificant photodemethylation and photoreduction in the presence of isoprene com-
418 pared to results without it (Table S12), revealed that $^3\text{NOM}^*$ were downplayed in MMHg pho-
419 tochemical process in none of the redox conditions. Furthermore, insignificant variation be-
420 tween k_{pr} under anoxic and oxic conditions in the Cont-ip experiment (Table S3), might under-
421 play the hypothesis of $^3\text{NOM}^*$ scavenging by O_2 . However, in the presence of VOCs, in the
422 Post-ip experiment, O_2 played as an inhibitor for the photodemethylation pathways driven by
423 LMW photosensitizers, which highlighted VOCs role. Moreover, DOM absorbance spectra of
424 the solution showed the highest absorbance for without short UVB wavelength range in anoxic
425 conditions and the lowest absorbance belonged to the solution irradiated under full light in
426 oxic conditions (Fig.S5). Similarly, Fig.S6 illustrates a decline for $\text{SUVA}_{\lambda=254\text{ nm}}$ values in oxic con-
427 ditions. Under anoxic conditions, lower DOM degradation can be explained through attenua-
428 tion of DOM photobleaching following O_2 removal from the solution (*Helms et al., 2008*). DOM
429 photobleaching process under oxic conditions would therefore be a reason why O_2 prohibited
430 MMHg photodemethylation by changing in the DOM photosensitization (*Niu et al., 2014*) and
431 finally fall of its capacity to assist in the intramolecular electron transfer from the chromo-
432 phoric groups.

433 **4.5 Environmental implication**

434 It is worth considering that in previous works, only MMHg concentration has been de-
435 termined in the solutions and the photodemethylation term was referred to the production
436 of iHg and $\text{Hg}(0)$. In our current work, for the first time, (i) three Hg species (MMHg, iHg, and
437 $\text{Hg}(0)$) were measured, (ii) VOCs measurement supported the production of organic interme-
438 diates from chromophoric DOM photolysis, and (iii) VOC's role was highlighted in MMHg pho-
439 tochemical pathways. Our results suggest a pathway for MMHg photodecomposition which is
440 following DOM photolysis, then production of reactive LMW organic compounds, and finally

441 direct intramolecular charge transfer within MMHg-DOM binding which led to direct photo-
442 dissociation of the C-Hg bond. The role of O₂ for both quenching photochemical energy (ROS
443 production) and resulting DOM photobleaching, is likely responsible for the lower MMHg pho-
444 todemethylation and photoreduction under oxic conditions. Normalized rate constants under
445 natural sunlight for specific wavelengths showed that the relative ratio is independent of the
446 O₂ level, suggesting O₂ is a simple inhibitor for photodemethylation process. Our results would
447 be implemented in observation of high MMHg photodemethylation in natural freshwaters un-
448 der suboxic conditions and high sunlight irradiation. For instance high MMHg photodemethy-
449 lation have been reported in subtropical Bolivian lake waters in high altitude, > 3600 m with
450 low O₂ concentration (*Bouchet et al., 2022*), and Pyrenean lake waters under important solar
451 irradiation (*Duval et al., 2023*). According our work, global warming and lakes eutrophication
452 can increase MMHg photodemethylation and iHg(II) photoreduction processes which may
453 have direct impacts on Hg turnover in aquatic ecosystems. These results will therefore im-
454 prove our understanding to interpret Hg species cycling and compare field data obtained for
455 example from eutrophic and oligotrophic freshwater. As previous works have mentioned that
456 MMHg affinity complexation by carboxyl ligands is significant but after that for thiol ligands
457 (*Yoon et al., 2005; Zhang et al., 2018*), further works are needed to determine whether these
458 dominant MMHg-thiol complexes would enhance photodemethylation and photoreduction
459 rate constants. This future work can probably illuminate thiol roles and determine the key
460 factors in the pathways of MMHg photodemethylation in freshwaters.

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462

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468

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686

687 **Figure Caption:**
688 Fig.1. The Hg species yield (MMHg, iHg remained in solution and trapped gaseous Hg(0)) rela-
689 tive to the absorbed energy during photodemethylation and photoreduction under full light
690 (a), without short UVB (b), PAR light (c) for the post-irradiation purging (Post-ip) experiment,
691 and under full light (d), without short UVB wavelength (e), PAR light (f) for the continuous-
692 irradiation purging (Cont-ip) experiment in anoxic (solid lines) /oxic (dashed lines) conditions.