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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 ± 2.2 kJ^{-1} compared to oxic conditions at 4.5 ± 0.4 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 $K_{pd\ PAR}$: $K_{pd\ long\ UVB+\ UVA}$: $K_{pd\ short\ UVB}$ at 1: 74: 999, and 1:182:977 for anoxic and oxic conditions, respectively, demonstrate that the relative ratio is independent of the O_2 level, meaning O_2 is a simple inhibitor for photodemethylation process. The comparison

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

Keywords

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

1. INTRODUCTION

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

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

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

Fantozzi et al., (2007) pointed out that some chromophoric group in DOM plays an important role in Hg(0) production owing to the complexation of iHg to the carboxyl groups in organic matter and, thereby promoting the light-induced production of Hg(0). Another work showed that the photoreduction rate is affected not only by the functional groups such as -OH and -COOH on the aromatic cycles but also by the position of these functional groups on the ring structure (*He et al., 2012*). A strong correlation between UV absorption of DOM molecules and DOM concentrations led to suggest that iHg photoreduction results from the DOM photolysis and the subsequent formation of high ROS production and intramolecular electron transfer via Hg complexation to photoreactive DOM (*Han et al., 2017; He et al., 2012; Tai et al., 2014; Whalin et al., 2007*). MMHg photodemethylation rate is influenced by competition between complexation reagents to MMHg (*Tai et al., 2014*). For instance, reduced DOM (low oxidation state) participates in photodemethylation 3 times faster than oxidized DOM (*Qian et al., 2014*). These authors indicated that MMHg photodemethylation process requires a synergic effect between strong binding MMHg- ligand i.e., thiol (*Chandan et al., 2015*) and direct energy transfer from photoreactive moieties such as aromatic cycles to break the Hg-C bonds (*Qian et al., 2014*). In addition, water components such as chloride (Cl^-), nitrate (NO_3^-), and iron (Fe(III)) are important factors in affecting substantially the photodemethylation rate (*Sun et al., 2017*).

Under oxic conditions, various studies have given different conclusion about ROS involved in MMHg photochemical reactions that are summarized here: i) hydroxyl radicals ($^{\bullet}OH$) produced through photo-Fenton reactions (*Kim and Zoh, 2013*) or NO_3^- photolysis (*Chen et al., 2003; Kim and Zoh, 2013*), and its production can be enhanced by pH increase in freshwaters (*Kim et al., 2017; Kim and Zoh, 2013*) and ii) Singlet oxygen ($^1O_2$) which has been shown as a highly reactive photodemethylation driver (*Zhang and Hsu-Kim, 2010*). The suggested MMHg photochemical pathways can be summarized as i) direct photodissociation of the C-Hg bond (*Han et al., 2017; Inoko, 1981; Tai et al., 2014*); ii) indirect pathways involving ROS and free radicals induced by DOM photolysis reactions (*Chen et al., 2003; Hammerschmidt and Fitzgerald, 2010; Zhang, 2006; Zhang and Hsu-Kim, 2010*). Unlike the previous cited work, a study showed that the addition of various $^{\bullet}OH$, and $^1O_2$ scavengers did not result in a MMHg photodemethylation decrease (*Black et al., 2012*). These authors concluded that MMHg photodemethylation can occur via various pathways; and iii) direct photolysis via intramolecular

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

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

2. MATERIAL AND METHODS

Experimental design

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

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

All the experiments were performed in triplicate, and experimental uncertainty was calculated by standard deviations (SD) of triplicate samples. Two series of control experiments were performed under dark (wrapped reactors using aluminum foil) and without DOM, under the same conditions as described above. Under oxic conditions, role of ROS in the photodemethylation pathways was determined using three scavengers including isopropanol, isoprene, and sodium azide (NaN_3) as probes of $^{\bullet}OH$, triplet excited state dissolved natural organic matter ($^3NOM^*$), and $^1O_2$, respectively (*Buxton et al., 1988; Boreen et al., 2008; Miyoshi et al., 1982*). To test the reactivity of these scavengers to photoreactive intermediates species including ROS and reactive organic species, scavenger experiment was investigated under anoxic condition, whereby almost no O_2-drived ROS can be produced. In addition, iron chloride ($FeCl_3$) was used as a hydroquinone scavenger (*Jiang et al., 2015*) under two redox conditions. All steps of Hg species analyses, DOM characterization, ROS measurement, scavenger experiment, and calculation of photodemethylation and photoreduction rate constants are described in details in the Supplementary Information file.

3. RESULTS

3.1 Effect of redox condition on MMHg photodemethylation

In this work, the photodemethylation term is employed for the photochemical transformation of MMHg into iHg while photoreduction indicates the iHg photochemical reduction process to Hg(0). Three Hg species yields, MMHg%, iHg%, and gaseous Hg(0)% were normalized according to the total MMHg initially added into the solutions. The irradiation times (s) were converted to absorbed energy (J) using measured simulator irradiance (W cm^{-2}) and reactor's physical parameters (Supplementary Information, Section 3). No evidence of abiotic demethylation or reduction was observed in dark control experiment (Table S1). In post-irradiation purging (Post-ip) experiment, under full light with absorbed energy at 4J, MMHg was photodemethylated to 2±1% iHg, and 4±2% was photoreduced to Hg(0) under anoxic conditions whereas, under oxic conditions, MMHg was photodemethylated to 1±1% iHg and photoreduced to 1±0% Hg(0) (Fig.1a, Fig.S4a and Table S2). With absorbed energy increasing to 206J, iHg and Hg(0) proportions rose to 8±2% and 23±6%, respectively, under anoxic conditions. Whereas, under the oxic condition, 9±1% iHg and 6±0% Hg(0) were produced (Fig.1a, Fig.S4a and Table S2).

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

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

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

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

3.2 Effect of purging mode on MMHg photodemethylation

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

Under anoxic conditions, without short UVB with energy at 31J, MMHg was photodemethylated to 3±3% iHg and photoreduced to 2±0% Hg(0) (Fig.1e, Fig.S4e and Table S4). These Hg species proportions increased to 5±1% and 7±1%, respectively by increasing energy to 185J. Under oxic conditions, similar results to the Post-ip experiment (section 3.1) were again obtained meaning iHg and Hg(0) rose from 2±0% to 3±0% and from 1±0% to 5±0%, respectively, by energy increase from 8J to 192J.

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

oxic conditions, it presented insignificant variation, despite a higher variation in absorbed energy from 5J to 61J.

3.3 Chemical characterization of dissolved organic matter and light absorption

The Post-ip experiment showed insignificant MMHg photodemethylation and photoreduction without DOM under two redox conditions (Table S5). The solutions were characterized through i) cations, anions, and dissolved organic carbon concentration analyses (Tables S6 and S7), ii) measurement of UV-Visible spectra (280-800 nm) of remained solutions (Fig.S5), and iii) measurement of Volatile Organic Compounds (VOC with mass/ charge < 300) produced in pre-and post-irradiation solutions under anoxic and oxic conditions. Insignificant variation was observed in chemical elements concentrations regarding redox conditions (Table S6). The pH and Eh were measured at 6.3 and 230 mV in the initial solution, respectively. Under anoxic conditions, pH increased to 7.5 and Eh decreased to 90 mV in pre-irradiation solution. The pH decreased to 7.0 and Eh reached 130 mV in post-irradiation step at 39 J of absorbed energy. Under oxic conditions, in pre-, and post-irradiation steps, pH and Eh varied within a small range from 6.0 to 6.3 and from 210 mV to 230 mV, respectively. The UV-Visible spectra of remained solutions were measured from 280 nm to 800 nm (Fig.S5). Lower absorbances were observed in oxic conditions. From this dataset, the Specific UV Absorbance (SUVA) value was calculated at 254 nm wavelength representing the aromaticity and humification index of the DOM (Fig.S6, and Table S8). For a specific adsorbed energy, SUVA values confirmed the latter results meaning $SUVA_{Anoxic- No\ short\ UVB} > SUVA_{Anoxic-Full\ light} > SUVA_{Oxic-No\ short\ UVB} > SUVA_{Oxic-Full\ light}$ for both Post-ip and Cont-ip experiments (Fig.S6). The SIFT-MS analyses in pre-irradiation samples showed two matrices with VOCs content under anoxic and oxic conditions (Fig.S7). The presence of five identical VOCs was confirmed in the pre-irradiation steps under anoxic and oxic conditions (Table S9). These VOCs presented mass to charge ratio (m/z) at 57, 73, and 211 for precursor O^{2+}, and 62, and 130 for precursor OH^-. In the post-irradiation step, the SIFT-MS analyses revealed production of various VOCs under anoxic and oxic conditions (Fig.S8). The m/z ratios and intensities of these VOCs were listed in Table S10. SIFT-MS analyses showed production of phenolate with m/z ratio at 93 for precursor O_2^- in pre-and post-irradiation samples under anoxic conditions. Moreover, the appearance of propanal and acetaldehyde was detected in the pre-and post-irradiation steps under both redox conditions (Table S10).

3.4 Measurement of potential production of reactive oxygen species

Results of the ROS analyses showed a higher potential production of HTA as probe of $^{\bullet}OH$, under anoxic conditions than oxic conditions (Fig.S9a). $^{\bullet}OH$ production increased four-fold under anoxic compared to oxic conditions. A similar result was obtained for XTT absorbance measurement indicating four-fold higher potential production of superoxide radical ($O_2^{\bullet-}$) under anoxic compared to oxic conditions (Fig.S9b, and Table S11). Under oxic conditions, insignificant variations were observed for the iHg and Hg(0) production in the presence of isoprene, and isopropanol compared to the experiment without scavenger (Table S12 and Fig.S10). Addition of sodium azide slightly inhibited MMHg photodegradation for 7% and led to production of 2±1% iHg and 6±1% Hg(0). Although, sodium azide is well-known as $^1O_2$ under oxic conditions, it surprisingly inhibited photodemethylation and photoreduction by the production of 7±1% iHg and 1±0% Hg(0), under anoxic conditions. Under anoxic conditions, the addition of isoprene and isopropanol scavengers showed insignificant results in MMHg photodemethylation to iHg, and also photoreduction to Hg(0) compared to the experiment without scavengers. Iron(III) addition promoted MMHg photodemethylation up to 40±2% iHg whereas, it suppressed iHg photoreduction to Hg(0) at 18±2%.

4. DISCUSSION

4.1 A two-step mechanism of photodemethylation and photoreduction

In agreement with our work, an enhancement in MMHg photodemethylation was previously observed under anoxic compared to oxic conditions (*Pan et al., 2017*). A simple comparison between the Post-ip and Cont-ip experiments data, under the same conditions i.e., redox and wavelength, revealed the production of the same proportion of iHg with uncertainties consideration (Fig.1, and Tables S2 and S4). The most important outcome of this comparison confirms our hypothesis that MMHg photodecomposition is mainly induced by the first step of C-Hg bond cleavage meaning MMHg photodemethylation to iHg(II) and then followed by iHg(II) photoreduction step to Hg(0). The second outcome of these results showed that this process includes no back Hg(0) oxidation. Indeed, observation of higher Hg(0) production under anoxic conditions in the Post-ip experiment whereby Hg(0) can be oxidized to iHg, suggested that the iHg photoreduction step to Hg(0) is performed as an almost irreversible reaction and Hg(0) oxidation is negligible. Using Box Lucas 2 exponential fitting model and kinetic

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

4.2 Oxygen influences on photodemethylation and photoreduction

ROS implication in photodemethylation and photoreduction processes has been debated in several studies. On one side, some previous works presented ROS, including $^{\bullet}OH$ (*Chen et al., 2003; Hammerschmidt and Fitzgerald, 2010*) and $^{1}O_2$ (*Black et al., 2012; Kim et al., 2017; Suda et al., 1993; Zhang and Hsu-Kim, 2010*) as intermediate compounds responsible for photodemethylation and photoreduction, on the other side, several works showed that ROS has a minor role and MMHg photochemical reactions occur by intramolecular charge transfer by DOM (*Tai et al., 2014; Zhang et al., 2018*). Nevertheless, *Fernández-Gómez et al., (2013)* explained that ROS production is related to DOM photolysis, therefore DOM controls ROS production, and even an increase in DOM can quench ROS and limits MMHg photodemethylation as shown by *Kim and Zoh, (2013)*. DOM reactivities in two redox condition are subject of the following discussion in section 4.4.

According to literature, $^{\bullet}OH$ production can result from two processes: i) photolysis of nitrogen-containing DOM (*Vione et al., 2006; Warneck and Wurzinger, 1988*), and ii) photo-Fenton process enhancement because of DOM and Fe interactions (*Voelker and Sulzberger, 1996*). Although an experimental study has shown $^{\bullet}OH$ production from the photolysis of NO_3^- enables MMHg photodemethylation (*Chen et al., 2003*), another experimental study in surface coastal waters has contradicted and reported that NO_3^- concentration does not control photodemethylation (*DiMento and Mason, 2017*). However, average NO_3^- and Fe(III) concentrations were measured herein in the solutions at 9 µmol L^{-1} and 0.2 µmol L^{-1}, respectively (Table S6) , both lower than reported values ($NO_{3\ our\ work}^- < 620$ µmol L^{-1} *Chen et al., 2003*, and $Fe_{our\ work} < 2$ µmol L^{-1} *Voelker and Sulzberger, 1996*) which affected MMHg photodemethylation. Our ROS measurements seem to indicate higher potential production of $^{\bullet}OH$ and $O_2^{\bullet-}$ under anoxic conditions (Fig.S9). It should be noted that $^{\bullet}OH$ and $O_2^{\bullet-}$ production requires O_2 occurrence which was negligible under anoxic conditions (Eh=90mV) and also ROS production is expected to increase under oxic conditions and decrease under anoxic conditions (*Kong and Zepp, 2012; Xu et al., 2011*). ROS that have been often recognized as a critical factor in MMHg photodemethylation pathways (*Black et al., 2012; Chen et al., 2003; Hammerschmidt and Fitzgerald, 2010; Zhang, 2006; Zhang and Hsu-Kim, 2010*), while they do not play an important

role in MMHg photodegradation under our conditions. In addition, these results raise the question on the selectivity of XTT and HTA probes (*Šnyrychová & Hideg, 2008; Sutherland & Learmonth, 1997*) for these two ROS species and their reactivities against other reactive organic species produced by DOM photolysis e.g., low molecular weight (LMW) carbonyl groups of amino acids (*Bertilsson and Tranvik, 2000; Kieber and Blough, 1990; Kieber et al., 1990*). Since insignificant differences in photodemethylation and photoreduction were also found with and without isopropanol under oxic and anoxic conditions (Table S12), $^{\bullet}OH$ role in MMHg photodemethylation was downplayed. However, results showed remarkable inhibition of photodemethylation and photoreduction by NaN_3, suggesting that $^1O_2$ was partly responsible for photodemethylation and photoreduction under anoxic and oxic conditions (Table S12). Although NaN_3 was recognized as a $^1O_2$ scavenger in photocatalytic reactions (*Gao et al., 2019; Kim et al., 2017; Nosaka and Nosaka, 2017; Zhang et al., 2017*), adding NaN_3 with a concentration > 100 mmol L^{-1} showed a significant inhibition effect on the formation of MMHg-DOM complexes up to 50% (*Han et al., 2017*). Furthermore, a previous study has proven that $^1O_2$ cannot be involved in MMHg photodemethylation as a primary driver (*Tai et al., 2014*). They observed insignificant variation in MMHg photodemethylation rate by adding MoO_4^{2-}/H_2O_2, as a $^1O_2$ generator. It is also worth to mention that a previous study has shown N_3^- as efficient acceptors of carbon radicals (*Minozzi et al., 2009*). Either N_3^- suppresses MMHg-DOM complexation, or it interacts with organic carbon radicals, inhibition of MMHg photochemical reactions by N_3^- under anoxic and oxic conditions cannot be consequently interpreted as an effect of $^1O_2$ on these reactions. This supports the hypothesis of the production of other types of photosensitive intermediates such as reactive organic species (discussed in section 4.4) with similar reactivities as ROS toward XTT, TA, and N_3^-. Therefore, based on our specific approach comparing oxic and anoxic conditions, we can suggest that neither $^{\bullet}OH$ nor $^1O_2$ play a role in MMHg photodemethylation and iHg photoreduction reactions under such conditions.

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

up to three-fold (*Pan et al., 2017; Tai et al., 2014*). Our results therefore suggest that O_2 presence inhibits probably MMHg phototransformation processes. This finding confirm the experimentally hypothesis suggesting that O_2 may serve as a scavenger of some intermediates species for this process (*Tai et al., 2014*).

4.3 Role of ultraviolet light on photodemethylation and photoreduction

Normalized results of MMHg photochemical reactions rate constants under natural sunlight confirmed higher K_{pd} and K_{pr} under short UVB (Table 1). Several studies have previously determined the relative wavelength effects of UVB, UVA, and PAR on the MMHg photodemethylation with a UV radiation contribution > 70% (*Black et al., 2012; DiMento and Mason, 2017; Fernández-Gómez et al., 2013*). Although UVA has been recognized as responsible for photodemethylation in seawaters (*DiMento and Mason, 2017; Zhang and Hsu-Kim, 2010*), PAR contribution dominates in turbid waters (estuarine and wetland) because of the more rapid attenuation of UV light across the water column with high DOM concentration (*Black et al., 2012*). However, our results showed slight photodemethylation (e.g. $K_{pd\ PAR} < 0.4\ kJ^{-1}$) and photoreduction (e.g. $K_{pr\ PAR} < 20\ J^{-1}$) whatever redox conditions (Table 1), suggesting important influence of UV light on photodemethylation and photoreduction reactions. The relative ratio 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 oxic conditions under natural sunlight, respectively. These high relative ratios under oxic compared to those under anoxic conditions are related to the lowest $K_{pd\ PAR}$ at 0.1 kJ^{-1} under oxic conditions. Similar ratios have been reported at 1:43:3100, and 1:37:400 for $K_{pd\ PAR}$: $K_{pd\ UVA}$: $K_{pd\ UVB}$ in lake-wetland waters, under oxic conditions (*Black et al., 2012; Fernández-Gómez et al., 2013*). The disagreement can be referred to variation in wavelength ranges, light irradiance, DOM composition, and O_2 concentration in waters. A different result of the relative ratio of $K_{pr\ PAR}$: $K_{pr\ long\ UVB+\ UVA}$: $K_{pr\ short\ UVB}$ at 1:853:10887, and 1:1810:9651 was obtained for anoxic and oxic conditions under natural sunlight, respectively (Table 1). These high relative ratios are related to the negligible normalized values of $K_{pr\ PAR}$ at 20 and 4 J^{-1} in anoxic and oxic conditions under natural sunlight, respectively. These latter relative ratios showed a major role of UV light in the order: short UVB > long UVB+UVA in the photoreduction reaction, regardless redox conditions.

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

The main factor influencing DOM photoreactivity between two redox conditions might result from the production of various reactive organic compounds. In post-irradiation step, a comparison of VOC measurement results revealed production of different VOCs with mass/charge < 300 through DOM photolysis in oxic and anoxic conditions (Table S10). These results are consistent with previous works that have shown higher photodemethylation rate in the presence of LMW organic matter, i.e. < 3.5 kDa due to the high photosensitization efficiency (*Kim et al., 2017; Tai et al., 2014; Zhang et al., 2017*). Production of phenolate as one of the VOCs which was detected only in anoxic conditions confirmed difference in DOM reactivity following photolysis under various redox conditions. These results suggested the contribution of phenolate (and similar derivatives) as a reactive chromophore in photodemethylation and photoreduction in anoxic conditions. According to pK_a of phenol at 7.2 (*Zhu et al., 2000*), during anoxic condition when pH of the solution goes beyond its pK_a i.e. 7.5, phenols exists as negative phenolate which was detected by VOC measurement. SRFA contains abundant LMW functional groups, such as phenols (*Zhang et al., 2018*, Table S13) or hydroquinone (*Zheng et al., 2012; Fleck et al., 2014; Ratasuk and Nanny, 2007*) which can participate in iHg photoreduction via intramolecular electron through UV-light absorption (at 288 nm, *Sirajuddin et al., 2007*) and photoexcitation (*Zheng et al., 2012*). Under oxic conditions, phenol was hydroxylated in para positions, yielding hydroquinone (*Andrade et al., 2006; Quintanilla et al., 2006; Santos et al., 2002*) which was immediately oxidized to quinone in the presence of O_2 (*Lerner et al., 2006*), whereas under anoxic conditions, phenol hydroxylation and hydroquinone oxidation were prevented due to lack of $^{\bullet}OH$ and O_2. In our work, adding Fe(III) as hydroquinone scavenger proved their role in iHg photoreduction (Fig.S10 and Table S12). Under oxic conditions, Fe inhibits iHg photoreduction by scavenging hydroquinone moieties and its oxidation to quinone (*Jiang et al., 2015*) and finally suppresses its participation in photoreduction, whereas under anoxic conditions, oxidation of hydroquinone by Fe was prevented because of the lack of O_2. These data highlighted phenol and hydroquinone roles in iHg photoreduction reaction in anoxic conditions. The importance of LMW organic compounds for MMHg photodemethylation and photoreductions processes was revealed through a compar-

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

In a previous work, *Pan et al.,* (*2017*) explained a high photodemethylation rate observed under anoxic conditions through ^{3}NOM* scavenging by O_2 under oxic condition. However, insignificant photodemethylation and photoreduction in the presence of isoprene compared to results without it (Table S12), revealed that ^{3}NOM* were downplayed in MMHg photochemical process in none of the redox conditions. Furthermore, insignificant variation between k_{pr} under anoxic and oxic conditions in the Cont-ip experiment (Table S3), might underplay the hypothesis of ^{3}NOM* scavenging by O_2. However, in the presence of VOCs, in the Post-ir experiment, O_2 played as an inhibitor for the photodemethylation pathways driven by LMW photosensitizers, which highlighted VOCs role. Moreover, DOM absorbance spectra of the solution showed the highest absorbance for without short UVB wavelength range in anoxic conditions and the lowest absorbance belonged to the solution irradiated under full light in oxic conditions (Fig.S5). Similarly, Fig.S6 illustrates a decline for $SUVA_{\lambda=254\ nm}$ values in oxic conditions. Under anoxic conditions, lower DOM degradation can be explained through attenuation of DOM photobleaching following O_2 removal from the solution (*Helms et al., 2008*). DOM photobleaching process under oxic conditions would therefore be a reason why O_2 prohibited MMHg photodemethylation by changing in the DOM photosensitization (*Niu et al., 2014*) and finally fall of its capacity to assist in the intramolecular electron transfer from the chromophoric groups.

4.5 Environmental implication

It is worth considering that in previous works, only MMHg concentration has been determined in the solutions and the photodemethylation term was referred to the production of iHg and Hg(0). In our current work, for the first time, (i) three Hg species (MMHg, iHg, and Hg(0)) were measured, (ii) VOCs measurement supported the production of organic intermediates from chromophoric DOM photolysis, and (iii) VOC's role was highlighted in MMHg photochemical pathways. Our results suggest a pathway for MMHg photodecomposition which is following DOM photolysis, then production of reactive LMW organic compounds, and finally

direct intramolecular charge transfer within MMHg-DOM binding which led to direct photodissociation of the C-Hg bond. The role of O_2 for both quenching photochemical energy (ROS production) and resulting DOM photobleaching, is likely responsible for the lower MMHg photodemethylation and photoreduction under oxic conditions. Normalized rate constants under natural sunlight for specific wavelengths showed that the relative ratio is independent of the O_2 level, suggesting O_2 is a simple inhibitor for photodemethylation process. Our results would be implemented in observation of high MMHg photodemethylation in natural freshwaters under suboxic conditions and high sunlight irradiation. For instance high MMHg photodemethylation have been reported in subtropical Bolivian lake waters in high altitude, > 3600 m with low O_2 concentration (*Bouchet et al., 2022*), and Pyrenean lake waters under important solar irradiation (*Duval et al., 2023*). According our work, global warming and lakes eutrophication can increase MMHg photodemethylation and iHg(II) photoreduction processes which may have direct impacts on Hg turnover in aquatic ecosystems. These results will therefore improve our understanding to interpret Hg species cycling and compare field data obtained for example from eutrophic and oligotrophic freshwater. As previous works have mentioned that MMHg affinity complexation by carboxyl ligands is significant but after that for thiol ligands (*Yoon et al., 2005; Zhang et al., 2018*), further works are needed to determine whether these dominant MMHg-thiol complexes would enhance photodemethylation and photoreduction rate constants. This future work can probably illuminate thiol roles and determine the key factors in the pathways of MMHg photodemethylation in freshwaters.

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Figure Caption:

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