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# Mechanistic elucidation of abiotic monomethylmercury photodemethylation in freshwaters: Experimental evidence

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**Mechanistic elucidation of abiotic monomethylmercury photodemethylation in freshwaters: Experimental evidence**

Inorganic mercury (iHg) and monomethylmercury (MMHg) can accumulate in aquatic organisms and MMHg biomagnifies along the trophic chain, presenting a hazard to higher consumers, including humans. The MMHg decomposition can be abiotically induced by photodegradation in the water column or biotically by certain microorganisms. Our aim in this work was to elucidate the abiotic photodemethylation pathway in model freshwater (Fulvic Acids organic matter – SRFA with DOC=6ppm, and [MMHg]=50 ppb at pH 6.5). We, therefore, irradiated MMHg freshwater solution through exposure to the solar spectrum (e.g. 280-800 nm) and performed kinetic experiments following Hg species concentrations (iHg(II), MMHg, Hg(0)). Dissolved gaseous mercury (Hg(0)) was trapped continuously purging with pure air and/or Argon (Ar). The role of oxygen was evaluated for MMHg photodemethylation rate and Hg(0) photo-oxidation. In addition, reactive oxygen species (ROS) production was evaluated by chemical quenching tests; and mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) of Hg stable isotopes (expressed as $\delta^{202}$Hg, and $\Delta^{199}$Hg), were measured in the freshwater solution.

In all experiments, >50% of photodemethylated MMHg was transformed to Hg(0), regardless of purging gas. Unexpectedly, photodemethylation under Ar showed a higher kinetic rate and Hg(0)/iHg(II) ratio than those with air saturation. Moreover, ROS test showed higher production of radical species under Ar. This experiment rejects the hypothesis of enhanced Hg(0) oxidation with higher $O_2$ content. It also suggests that the occurrence of high $O_2$ concentration may inhibit photodemethylation, preventing electron transfer between organic matter and/or redox-sensitive couples (i.e. iron). MMHg photodemethylation showed MDF within the range $\delta^{202}$Hg + 0.25 - + 0.30 ‰. Photodemethylation in Ar resulted in larger MIF with $\Delta^{199}$Hg = 3.1 ‰, whereas, under air, MIF reached 1.7 ‰. Therefore, high Hg(0)/iHg ratio during photodemethylation in Ar confirms that large MIF resulted from a complete photodemethylation and/or photoreduction of iHg(II) to Hg(0) pathways. This study highlights the role of oxygen in the inhibition of the photochemical pathways. These competitive mechanisms influence in turn the isotopic fractionation extent of Hg (MIF). The role of organic radicals and overlooked redox species will be further discussed.