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Photolytic degradation of methylmercury enhanced by binding to natural organic ligands

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Abstract

Monomethylmercury is a neurotoxin that poses significant risks to human health¹ due to its bioaccumulation in food webs. Sunlight degradation to inorganic mercury is an important component of the mercury cycle that maintains methylmercury at low concentrations in natural waters. Rates of photodecomposition, however, can vary drastically between surface waters^{2–5} for reasons that are largely unknown. Here, we show that photodegradation occurs through singlet oxygen, a highly reactive form of dissolved oxygen generated by sunlight irradiation of dissolved natural organic matter. The kinetics of degradation, however, depended on water constituents that bind methylmercury cations. Relatively fast degradation rates (similar to observations in freshwater lakes) applied only to methylmercury species bound to organic sulfur-containing thiol ligands such as glutathione, mercaptoacetate, and humics. In contrast, methylmercury-chloride complexes, which are dominant in marine systems, were unreactive. Binding by thiols lowered the excitation energy of the carbon-mercury bond on the methylmercury molecule^{6–7} and subsequently increased reactivity towards bond breakage and decomposition. Our results explain methylmercury photodecomposition rates that are relatively rapid in freshwater lakes^{2–4} and slow in marine waters⁵.

Demethylation of methylmercury (MeHg) in natural waters occurs through both biological^{8–9} and photochemical processes³. In sunlit waters, the photochemical process is the dominant removal pathway and has been estimated to account for as much as 80% of MeHg flux out of lakes^{3,10}. While sunlight is known to induce MeHg degradation, rates vary among different types of water. Photodegradation is rapid in remote lakes in North America and the Arctic^{2–4}, but relatively slow in seawater, especially compared to microbial processes⁵. The reason for such variability is unknown because the photodemethylation process is poorly understood.

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Author contributions

T.Z. performed all experiments and data analysis. H.H. conceived the study, supervised the research, and performed speciation calculations. Both authors drafted the manuscript.

Competing Financial Interests

The authors have no competing financial interests.

MeHg degradation is likely to be induced by the ultraviolet spectrum (<400 nm) of sunlight². Hydroxyl radicals ($\cdot\text{OH}$), which are produced via photo-Fenton reactions or by photolysis of nitrate, have been proposed as the reactive intermediates responsible for photodegradation^{11–12}. However, with previously reported $\cdot\text{OH}$ demethylation rates ($k \sim 2$ to $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)^{11–13}, significant MeHg degradation by this pathway would require large steady state $\cdot\text{OH}$ concentrations that would occur only under specific conditions: agriculturally-impacted waters (with high nitrate and low dissolved organic carbon^{13–14}) or in acidic waters (pH ≤ 6) with sufficient soluble Fe to drive photo-Fenton processes¹⁵. While production of $\cdot\text{OH}$ is possible at neutral pH¹⁶, production rates are highly sensitive to pH shifts, dissolved natural organic matter (NOM) content, and filtration of samples (in which removal of particulate Fe-oxides would decrease $\cdot\text{OH}$ production). Such patterns are inconsistent with previous field studies on MeHg photodegradation in which pH variations (from 6 to 7.5) and filtration of the sample did not change photodegradation rates^{2–4, 10}. Such discrepancies point to another photoreactive intermediate (in addition to $\cdot\text{OH}$) that can induce MeHg degradation in surface waters.

MeHg degradation can also occur through singlet oxygen ($^1\text{O}_2$)¹⁷, which is generated by sunlight sensitization of dissolved NOM^{18–19}. Here, we show that reaction rates between $^1\text{O}_2$ and MeHg are sufficient to account for sunlight-induced degradation. However, these rates apply only to certain types of MeHg species in water: CH_3Hg -thiol complexes with NOM.

We performed photodegradation experiments in a simulated freshwater containing MeHg, Suwannee River humic acid, and a phosphate buffer (pH 7 to 7.4). In two separate experiments, sample containers (Teflon FEP) were exposed to natural sunlight over 4 days in October and December 2008 on a building roof top in Durham, North Carolina. During the exposure period, MeHg did not degrade in appreciable amounts in samples that contained only the phosphate buffer (Figure 1a). MeHg degradation was observed only when humic acid was present and when the MeHg concentration was low (15 nM) relative to humic acid. The differences observed between the 15 nM and 1500 nM MeHg treatments could be caused by complexation between MeHg and thiols associated with the humic. In the sample with 2 mg-C/L humic, the reduced-sulfur concentration from the humic acid was estimated at 150 nM (assuming 7.3×10^{-5} moles reduced-S per g C^{20}) and greater than total MeHg (15 nM). In contrast, the sample with 1.1 mg-C/L humic and 1500 nM MeHg contained 80 nM reduced-S, less than MeHg concentration.

We performed similar photodegradation experiments using a laboratory UV-A reactor ($\lambda = 365 \text{ nm}$) to show that degradation rates depended on the concentration of MeHg relative to humic acid. MeHg degradation occurred only if humic acid was present (Supplementary Figure S1). Furthermore, degradation was observed only at MeHg concentrations (0.5 nM and 125 nM) that were less than the estimated reduced-S content of the humic (200 nM) (Figure 1b). We observed similar trends demonstrating the concentration dependence for MeHg degradation in samples formulated in seawater (Supplementary Figure S1). The UV-B component of the solar spectrum may also contribute to photodegradation² but was not tested in our study.

Sunlight irradiation of chromophoric NOM is known to generate reactive intermediates such as $\cdot\text{OH}$, superoxide, and $^1\text{O}_2$ ²¹. In additional photodegradation experiments, we utilized selective probes to identify the reactive intermediate that was responsible for MeHg decomposition (Figure 2). The addition of β -carotene and sodium azide (NaN_3), which are probes for $^1\text{O}_2$, resulted in slower MeHg degradation kinetics (Figure 2a). Experiments were also repeated in 98.5% deuterated water (D_2O), a solvent that is ~ 13 times slower than H_2O at quenching singlet oxygen^{19,22} and thus, increases steady state $^1\text{O}_2$ levels. The use of D_2O appeared to increase the rate of decomposition; however, this enhancement was smaller than expected. The addition of isopropyl alcohol (a probe for $\cdot\text{OH}$ ²³) and isoprene (a probe for photosensitized triplet state NOM^{23–24}) did not appreciably change photodegradation rates (Figure 2b). MeHg degradation was not observed in dark controls: the recovery of MeHg was 92% ($\pm 8.3\%$) after 120 hr. Additional dark experiments with enzyme-generated superoxide indicated that superoxide was not capable of decomposing MeHg within this time frame (Supplementary Figure S2). Collectively these results suggested that $^1\text{O}_2$ was the reactive intermediate responsible for photodegradation in our experiments and not other types of intermediates such as $\cdot\text{OH}$, photosensitized NOM, and superoxide.

The experiments with β -carotene, NaN_3 , and D_2O demonstrated the consequence of a heterogeneous distribution of $^1\text{O}_2$ in humic acid solutions and the binding of MeHg to NOM. According to Latch and McNeill¹⁹, singlet oxygen is generated in the light-absorbing regions of dissolved NOM and quickly quenched by water. Therefore, the steady state $^1\text{O}_2$ concentration can be orders of magnitude greater in close proximity to dissolved NOM molecules than in bulk solution¹⁹. In our experiments, this concentration gradient may explain why hydrophilic modifiers such as NaN_3 and D_2O had less effect on MeHg degradation rates than would be predicted based on known reaction rates between the modifiers and $^1\text{O}_2$ (Supplementary Table S1). In contrast, β -carotene is a hydrophobic modifier that sorbed to NOM macromolecules and subsequently inhibited MeHg degradation to an extent that was predicted (Table S1). These results indicated that MeHg was sorbed to or complexed by humic molecules and, consequently, reacted with $^1\text{O}_2$ molecules in the hydrophobic regions of the NOM.

In our experiments water composition was an important factor controlling degradation kinetics. Rates depended on the relative concentrations of MeHg and humic acid (Figure 1). Direct interactions between MeHg and NOM (such as metal-ligand complexation) may be critical to photodemethylation kinetics.

We tested the importance of complexation by quantifying second-order rate constants $k_{^1\text{O}_2, \text{CH}_3\text{HgL}}$ for reactions between $^1\text{O}_2$ and CH_3Hg^+ -ligand complexes. Glutathione (GSH) and mercaptoacetate (MA) were selected as surrogates of thiol-containing ligands that are expected to bind to CH_3Hg^+ ions in NOM-containing freshwater^{25–26}. Cl^- and OH^- ligands are relevant for saline or low-NOM water. Singlet oxygen was generated by UV-A irradiation of rose bengal. Dark controls were also performed to ensure that the reactants did not cause degradation (Supplementary Figure S3). Additional experiments with amendments (D_2O or NaN_3) and with Eosin-Y (instead of rose bengal) were performed to demonstrate that singlet oxygen, and not sensitized rose bengal, was the reactive intermediate for the degradation experiments (Supplementary Figure S4). Reaction rate constants were

quantified by competition kinetics in which the simultaneous degradation of 2-chlorophenol was monitored in the same solution.

In water containing GSH and MA, we observed faster MeHg decomposition by $^1\text{O}_2$ than in water containing Cl^- or the phosphate buffer alone (Figure 3a). We observed similar trends in experiments with seawater (Supplementary Figure S5). These results indicated that $^1\text{O}_2$ -induced degradation was faster for CH_3Hg -GSH and CH_3Hg -MA complexes than for CH_3HgCl and $\text{CH}_3\text{HgOH}/\text{CH}_3\text{HgHPO}_4^-$ complexes (corresponding to PO_4 -buffered water with no additional ligands).

Complexation of sulfhydryl groups by mercury was expected to slow thiol oxidation by reactive oxygen species²⁷. However, the total thiol concentration was in excess of total Hg in the samples. Thus, the thiols were decomposing simultaneously during the reaction (Supplementary Figure S6), producing compounds such as organic sulfur radicals that may be capable of inducing demethylation. We tested the reactivity of thiol oxidation products by performing dark experiments with hydrogen peroxide (H_2O_2), which oxidized GSH and MA to form sulfhydryl radical intermediates²⁸. Decomposition of CH_3Hg -GSH complexes was not observed, even as GSH (which was in excess of MeHg) was oxidized by H_2O_2 (Supplementary Figure S7). Therefore, we concluded that sulfhydryl radicals were not the cause of MeHg degradation.

Second-order rates constants (Table 1) calculated from the $^1\text{O}_2$ experiments indicated that $k^1_{\text{O}_2, \text{CH}_3\text{HgL}}$ values for CH_3Hg -GSH and CH_3Hg -MA complexes were 2 to 4 times greater than the rate constant measured for the $\text{CH}_3\text{HgOH}/\text{CH}_3\text{HgHPO}_4^-$ mixture. Degradation of CH_3HgCl was not detected for the time scale of our experiments (34 hr). Thus, the CH_3HgCl rate constant with $^1\text{O}_2$ was at least an order of magnitude slower. For the $^{\bullet}\text{OH}$ degradation pathway, rate constants did not appear to differ between CH_3Hg -thiol complexes and $\text{CH}_3\text{HgOH}/\text{CH}_3\text{HgHPO}_4^-$ mixed speciation (Table 1).

The increased reactivity between CH_3Hg -thiol complexes and $^1\text{O}_2$ may be caused by shifts in carbon-mercury bond energies induced by thiol complexation. In theoretical studies, Ni et al.⁶ demonstrated that coordination of a reduced sulfur residue ($-\text{SH}$) to CH_3Hg^+ resulted in greater electronegativity at the carbon atom (and presumably increased reactivity with electrophiles). Tossel⁷ also utilized quantum mechanical calculations to show that sulfhydryl coordination decreased electron transition energies to a range where irradiation by low UV wavelengths ($\lambda < 270$ nm) could induce demethylation.

We confirmed these theoretical calculations by performing direct photolysis experiments with UV-C radiation ($\lambda = 254$ nm) to demonstrate that thiol complexation alters electron transition energies of the CH_3Hg -ligand molecule. Degradation of MeHg by UV-C was observed only if methylmercury was in the form of CH_3Hg -GSH complexes (Figure 3b). Degradation was not observed in the phosphate buffer alone, where methylmercury consisted of 90% CH_3HgOH and 10% $\text{CH}_3\text{HgHPO}_4^-$. Moreover, the observed decomposition rates increased as the GSH:MeHg molar ratio increased from zero to 1, and remained constant for all mixtures where GSH was in excess of MeHg. GSH did not decompose during direct UV-C exposure ($91.9\% \pm 1.4\%$ GSH recovered after 2600 mJ/cm^2).

fluence). These results showed that GSH complexation altered the reactivity of the MeHg molecule to make it more susceptible to photodegradation.

Speciation-dependent MeHg degradation rates can explain the variability observed between freshwater lakes and seawater. MeHg speciation differs greatly in these two ecosystems due to ligand competition between Cl^- and thiolate (R-S^-) functional groups associated with NOM. CH_3HgCl complexes are expected to be the major species in coastal marine waters with Cl^- concentration greater than 0.1 M (Supplementary Figure S8). In contrast, most freshwater systems contain enough dissolved NOM (>1 mg-C/L) and low Cl^- such that CH_3Hg^+ ions are bound to thiol ligands associated with NOM^{26, 29–30}.

In sunlit surface water containing NOM, the steady state concentration of $^1\text{O}_2$ can be as high as 10^{-13} to 10^{-12} M¹⁹. Using the CH_3Hg -thiol rate constants in Table 1, we calculated pseudo-first order photodegradation rates ranging from 0.04 to 0.6 d^{-1} , values that are close to rates quantified in lakes^{2–4}. Overall, our results indicate that ecosystem mass balances for MeHg must consider water composition and MeHg speciation when estimating losses from photodegradation. With this new understanding of how photodemethylation occurs, we can improve efforts to predict mercury cycling in the aquatic environment and prevent bioaccumulation of MeHg in food webs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Concentration dependence of MeHg photodegradation rates

a) MeHg degradation by sunlight in water containing Suwannee River humic acid (SRHA) and phosphate (1 mM, pH = 7). The high MeHg treatment (1500 nM) was exposed in October 2008 (15.2°C average noon temperature). The low MeHg treatment (15 nM) was exposed in December 2008 (8.9°C). Error bars represent ± 1 s.d. for replicate measurements ($n=2-3$) of the same sample. **b)** MeHg degradation by artificial UV-A ($\lambda=365$ nm) in water containing SRHA (2.8 mg-C/L) and phosphate (10 mM, pH 7.4). Data points represent the average MeHg concentration (± 1 s.d.) for duplicate samples.

Figure 2. MeHg degradation via generation of 1O_2 from photosensitized humic acid

MeHg was degraded by UV-A in simulated water containing MeHg (0.5 nM), SRHA (2.8 mg-C/L), and phosphate (10 mM, pH 7.3). **a)** Replicate samples were amended with either D₂O (a singlet oxygen enhancer), NaN₃ or β-carotene (singlet oxygen quenchers); **b)** No difference was observed in replicates amended with isoprene (a quencher for triplet state dissolved NOM) or isopropyl alcohol (quencher for $^{\bullet}OH$). Error bars represent ± 1 s.d. for replicate measurements (n=2–3).

Figure 3. Effect of ligand complexation on degradation of MeHg

a) Singlet oxygen-induced degradation of MeHg (350 nM) complexed with GSH, MA, Cl^- , or $\text{OH}^-/\text{HPO}_4^{2-}$ in water containing 2-chlorophenol (40 μM) and phosphate (10 mM, pH=7.3). $^1\text{O}_2$ was generated by UV-A ($\lambda = 365$ nm) irradiation of rose bengal. Lines indicate model predictions from rate constants. Error bars represent ± 1 s.d. for replicate measurements ($n=2-3$); **b)** Direct UV-C ($\lambda = 254$ nm) degradation of MeHg at varying initial ratios of MeHg and GSH (4 μM initial MeHg, 1 mM phosphate, pH 7.4). Solid line indicates a linear regression of data for $[\text{GSH}]_0:[\text{MeHg}]_0 = 1$.

Table 1

Degradation rate constants for methylmercury complexes. Values represent average (± 1 standard deviation) of duplicate photochemical experiments at 25–26 °C.

MeHg species	$^1\text{O}_2$ -induced degradation $k_{^1\text{O}_2, \text{CH}_3\text{HgL}}$ ($\text{M}^{-1} \text{s}^{-1}$)	$^{\bullet}\text{OH}$ -induced degradation $k_{^{\bullet}\text{OH}, \text{CH}_3\text{HgL}}$ ($\text{M}^{-1} \text{s}^{-1}$)	Direct UV ($\lambda = 254 \text{ nm}$) degradation k_D (cm^2/mJ)
CH_3HgCl	$<0.32 \times 10^6$ ^(b)	NA	NA
CH_3HgOH , $\text{CH}_3\text{HgHPO}_4^-$ mix ^(a)	$1.9 (\pm 0.04) \times 10^6$	$1.9 (\pm 0.09) \times 10^9$	$<0.23 \times 10^{-4}$ ^(c)
$\text{CH}_3\text{Hg-GSH}$	$7.4 (\pm 0.2) \times 10^6$	$1.9 (\pm 0.04) \times 10^9$	$2.2 (\pm 0.02) \times 10^{-4}$
$\text{CH}_3\text{Hg-MA}$	$4.9 (\pm 0.5) \times 10^6$	NA	NA

^(a) The initial methylmercury speciation (in phosphate buffer) was 49% CH_3HgOH and 51% $\text{CH}_3\text{HgHPO}_4^-$ in the $^1\text{O}_2$ -induced degradation experiments ($\text{pH} = 7.3$), and 90% CH_3HgOH and 10% $\text{CH}_3\text{HgHPO}_4^-$ in the $^{\bullet}\text{OH}$ -induced and direct UV-C degradation experiments ($\text{pH} = 7.4$).

^(b) Calculated limit of quantification based on $>95\%$ of the initial MeHg measured in solution after exposure to UV-generated $^1\text{O}_2$ for the maximum duration of the experiment (34 hr).

^(c) Calculated limit of quantification based on $>94\%$ of the initial MeHg measured in solution after the maximum UV fluence ($2600 \text{ mJ}/\text{cm}^2$) for the experiment.

NA: Not available