#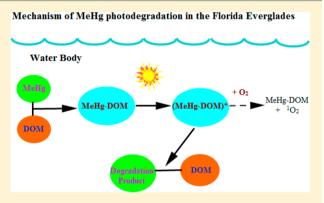 Methylmercury Photodegradation in Surface Water of the Florida Everglades: Importance of Dissolved Organic Matter-Methylmercury Complexation

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Ⓢ *Supporting Information*

**ABSTRACT:** Photodegradation is the major pathway of methylmercury (MeHg) degradation in many surface waters. However, the mechanism of MeHg photodegradation is still not completely understood. Dissolved organic matter (DOM) is expected to play a critical role in MeHg photodegradation. By using several techniques, including $N_2/O_2$ purging and the addition of stable isotope ($Me^{201}Hg$), scavengers, competing ligands, and a singlet oxygen ($^1O_2$) generator, the role played by MeHg−DOM complexation in MeHg photodegradation of Everglades surface water was investigated. DOM appeared to be involved in MeHg photodegradation via the formation MeHg−DOM complexes based on three findings: (1) MeHg was quickly photodegraded in solutions containing DOM extracts; (2) degradation of MeHg did not occur in deionized water; and (3) addition of competing complexation reagents (dithiothreitol-DTT) dramatically prohibited the photodegradation of MeHg in Everglades water. Further experiments indicated that free radicals/reactive oxygen species, including hydroxyl radical (·OH), $^1O_2$, triplet excited state of DOM ($^3DOM^*$), and hydrated electron ($e^-_{aq}$), played a minor role in MeHg photodegradation in Everglades water, based on the results of scavenger addition, $^1O_2$ generator addition and $N_2/O_2$ purging. A pathway, involving direct photodegradation of MeHg−DOM complexes via intramolecular electron transfer, is proposed as the dominant mechanism for MeHg photodegradation in Everglades water.


Mechanism of MeHg photodegradation in the Florida Everglades

## INTRODUCTION

Methylmercury (MeHg) is the most notorious form of mercury in the environment, and has drawn public concern due to its toxicity, bioaccumulation, and biomagnification through food webs.[1−3] In aquatic environments, MeHg is primarily formed by sulfate reducing bacteria[4] or iron reducing bacteria[5] in anoxic sediment, and sometimes by photomethylation in surface water.[6] In addition to methylation, degradation of MeHg also plays an important role in the biogeochemical cycling of mercury in aquatic ecosystems. This process may occur through a number of abiotic or biotic pathways.[7−9] Although microbial demethylation of MeHg was observed both in sediment[10] and in the water column,[11] most previous studies demonstrated that photodegradation is the major pathway of MeHg degradation in surface water.[12−14] It was reported that

photodegradation could remove a large proportion of the MeHg loading into lake water.[15,16]

Since its importance was demonstrated,[14] several researchers have attempted to mechanistically determine the MeHg photodegradation process in aquatic environments.[17−20] Although wavelength-specific photodegradation of MeHg has been observed in aquatic environments,[13,21] much remains unclear about the chemical processes governing MeHg photodegradation. Previous reports suggest three potential pathways are responsible for MeHg photodegradation: (1)

direct photodegradation of MeHg,[18] (2) photodegradation of MeHg-dissolved organic matter (DOM) complexes by free radicals/reactive oxygen species ($^1O_2$, triplet excited state of DOM ($^3DOM^*$), hydrated electron ($e^-_{aq}$), and $\cdot OH$),[19] and (3) photodegradation of MeHg not complexed with DOM by free radicals/reactive oxygen species.[20]

Direct photodegradation of MeHg species such as MeHgOH, and MeHgCl (pathway 1) ($\Delta E_{S-T}$ (Singlet−triplet excitation energies) 5.1−5.9 eV[22]) is theoretically difficult under solar radiation, as absorption by atmospheric ozone limits the solar spectrum at 4.4 eV.[23] Most experiments also suggest that MeHg could not be photodegraded in deionized water (DI water).[19,20] In the other two possible pathways (pathway 2 and 3), DOM could be involved because of its ability to produce free radicals/reactive oxygen species ($^1O_2$,[24,25] triplet excited state of DOM ($^3DOM^*$),[26,27] hydrated electron ($e^-_{aq}$),[28−30] and $\cdot OH$[31,32]) and to form MeHg−DOM complexes.[33] DOM should play a critical role in MeHg photodegradation.[17,19] Recent studies have demonstrated quick photodegradation of MeHg in solutions prepared with DOM isolated from wetlands[18] and rivers[19] under solar radiation. However, other studies proposed that $\cdot OH$ produced by the photo-Fenton reaction, without the involvement of DOM, could be the driver.[20] In addition to the disagreement of the importance of DOM, there is also a controversy on which free radicals/reactive oxygen species are involved in MeHg photodegradation.[19,20]

In most previous studies, $^1O_2$ or $\cdot OH$ were speculated to be the free radicals/reactive oxygen species driving the photodegradation of MeHg.[19,20] These conclusions were based mainly on the results of adding scavengers to remove various free radicals/reactive oxygen species[18−20] or measuring the degradation of MeHg in the presence of simulated $^1O_2$ or $\cdot OH$ generators.[19,20] These studies had several obvious shortcomings. First, although $^1O_2$ or $\cdot OH$ is commonly considered the free radicals/reactive oxygen species dominating MeHg photodegradation, none of these studies compared the difference of MeHg photodegradation under oxic and anoxic conditions, which is one of the important factors for confirming the importance of reactive oxygen species.[34,35] Second, there is a lack of studies evaluating the importance of $e^-_{aq}$, which is believed to be involved in the photodegradation of many pollutants.[29,30] Finally, although MeHg−DOM complexation was speculated to be critical for MeHg photodegradation,[19] there is a lack of evidence on the importance of this process in natural waters. In the past few years, several mechanisms have been proposed to drive the photodegradation of MeHg in surface waters, including $^1O_2$ induced degradation of MeHg−DOM complexes,[19] $\cdot OH$ (generated by photo-Fenton reaction) induced photodegradation,[20] and possible direct photodegradation.[18] The inconsistent outcomes of previous studies, conducted in different aquatic systems, indicate that the mechanism of MeHg photodegradation is still not completely understood.

The Everglades is a subtropical wetland ecosystem located in South Florida. Extensive studies have been carried out to understand the cycling of mercury in this ecosystem over the last two decades.[10,13,36−39] In our previous Everglades studies, photomethylation[40] and biotic degradation[13] in surface water was found to play a minor role in the cycling of MeHg. MeHg photodegradation was calculated to account for about 31% of the MeHg diffused from peat soils into the water column,[13] indicating the importance of photodegradation in MeHg cycling. The major objective of this study was to elucidate the pathways of MeHg photodegradation in Everglades surface water. To achieve this objective, stable isotope (Me$^{201}$Hg) addition technique was adopted to measure the rate of MeHg photodegradation under a variety of treatments. DOM extraction and competing ligand addition approaches were employed to test the importance of MeHg−DOM complexes in MeHg photodegradation. Scavenger addition, $^1O_2$ generator addition and $N_2/O_2$ purge experiments were utilized to determine the importance of the free radicals/reactive oxygen species in MeHg photodegradation.

## ■ MATERIALS AND METHODS

**Reagents.** MeHg standard was purchased from Ultra Scientific (N. Kingstown, RI). Enriched $^{201}$HgO and $^{199}$HgO (isotope purity, 96.17 ± 0.56%, and 91.09 ± 0.05%, respectively) were purchased from Oak Ridge National Laboratory (Oak Ridge, Tennessee) and used to synthesize enriched Me$^{201}$Hg and Me$^{199}$Hg using the methylcobalamin method.[13] Ultrahigh purity grade nitrogen and oxygen was used for degassing water. Other reagents used were of reagent or higher grade. Ultrapure water (>18 MΩ-cm) was used to prepare all chemical solutions.

**Measurement of MeHg Photodegradation Rate Constants under Various Treatments.** Surface water was collected from the Everglades (25°45′N, 80°44′W) 1 day before photodegradation experiments. All experiments were conducted under ambient solar radiation at Florida International University (25°45′N, 80°22′W), approximately 10 km from the sampling site. Me$^{201}$Hg was spiked into 500 mL of unfiltered surface water or extracted DOM solution placed in 500 mL fluorinated ethylene propylene (FEP) bottles to a final concentration of 1.0 ng L$^{-1}$. Samples were then incubated under ambient solar radiation (29.7−35.1 E m$^{-2}$ d$^{-1}$, average 32.4 E m$^{-2}$ d$^{-1}$) and temperature (20.0−31.9 °C, average 21.1 °C) for 6 days. During the experiment, intensity of ambient PAR was measured at 15 min intervals routinely using LI-192 Quantum Sensor (LICOR Biosciences, Lincoln, Nebraska). Triplicates (three separate bottles) were employed for each trial. An aliquot of water (35 mL) was taken from each bottle after 0, 1, 2, 4, 6 days of incubation. The aliquots were preserved to 1% concentrated HCl and then kept at 4 °C until analysis. Me$^{201}$Hg in the water samples was analyzed to calculate MeHg photodegradation rate constants (See Data Analysis). Details for Me$^{201}$Hg analysis can be found in the Supporting Information (SI).

**Influence of DOM Isolated from Everglades Water and Various Complexing Ligands on MeHg Photodegradation.** DOM (>3000 Da) was concentrated from filtered (0.22 μm, PTFE) Everglades water using a cross-flow ultrafiltration technique with a 3000 Da Millipore tangential flow filter membrane. The high molecular weight (HMW) DOM fraction was concentrated ~25 folds and washed 7 times with DI water to remove the low molecular weight (LMW) DOM and inorganic ions. Flocculation of DOM was not observed in HMW DOM when washing with DI water (possibly due to the near-neutral conditions, pH 6.7 in the water samples). The filtrates composed of low molecular weight DOM and ions were named as LMW. Concentrations of DOM and various ions in HMW and LMW fractions, and in Everglades water are shown in SI Table S1. The HMW fraction DOM was diluted 25 times to its original concentration in Everglades water prior to experimentation. Photodegradation
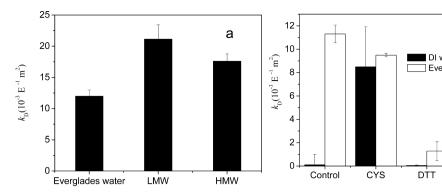
**Figure 1.** Importance of DOM−MeHg complexation in MeHg photodegradation. (a), Me[201]Hg photodegradation rate constants in >3000 Da DOM solution obtained from >3000 Da of Everglades water (HWM), Everglades water (control), and <3000 Da of Everglades water (LWM), (b) Me[201]Hg photodegradation rate constants in DI water and Eveglades water with the addition of various complexation ligands.

of Me[201]Hg in HMW and LMW solutions, and unaltered Everglades water was then measured.

To determine whether the complexation of MeHg with DOM plays an important role in MeHg photodegradation, various competing ligands of MeHg were added to Everglades' or DI water containing Me[201]Hg (1.0 ng L^{−1}). These competing ligands included cysteine (CYS) (10 mmol L^{−1}), and dithiothreitol (DTT) (10 mmol L^{−1}). CYS and DTT were chosen as the candidate competing ligands due to their high affinity for MeHg. Their complex stability constants with MeHg (log K) were 15.7, and 17.0, respectively and complexes of these ligands with MeHg were expected to be the major species of MeHg in Everglades water (99.99−100%, Table S3, see SI for calculation). MeHg photodegradation rate constants in these treatments were then determined.

**MeHg Photodegradation in Everglades Water in the Presence or Absence of $O_2$ and the Effects of Scavenger Addition.** To examine the importance of reactive oxygen species in MeHg photodegradation, MeHg photodegradation rate constants in Everglades water were measured with and without sparging with $N_2$ or $O_2$.

Scavengers for $^1O_2$, ·OH, $^3$DOM*, or $e^-_{aq}$, were added to surface water to achieve a concentration of 0−200 mmol L^{−1} (SI Table S2 for concentration increments of each scavenger). $NaN_3$ was chosen as the scavenger of $^1O_2$,[19] while isopropanol and dimethyl sulfoxide (DMSO) were selected as the scavengers of ·OH.[19,20] Isoprene was selected as the scavenger of $^3$DOM*,[19,20,41] while $N_2O$/isopropanol were used to scavenge $e^-_{aq}$.[42] Everglades water without adding any scavengers was included as a control. In addition, various concentrations of DMSO (10^{−4}-100 mmol L^{−1}), $NaN_3$ (0−200 mmol L^{−1}), and isoprene (0−20 mmol L^{−1}) were added to investigate the effects of scavenger concentrations on MeHg photodegradation. Triplicates (three separate bottles) were employed for each trial and control. MeHg photodegradation rate constants were measured using the method described above.

**MeHg Degradation in the Presence of $MoO_4^{2-}$/ $H_2O_2$ ($^1O_2$ Generator).** Me[201]Hg was spiked into 500 mL Everglades water to form a final concentration of 1.0 ng L^{−1} and the pH of the sample was adjusted to 10.4 with a $Na_2CO_3$ solution (10 mmol L^{−1}). $MoO_4^{2-}$ was then added into the solution to form a final concentration of 2 mmol L^{−1}. $H_2O_2$ (38%) was then added into the solution five times (2 mL every 2 h) in 10 h every day.[43,44] Samples were incubated in dark for 6 days and

Me[201]Hg concentrations on days 0, 1, 2, 4, and 6 were determined to calculate the degradation rate constants.

**Data Analysis.** *Calculation of MeHg Photodegradation Rate Constants.* A model based on second-order chemical kinetics was used to describe the photodegradation of MeHg in the water (eq 1).[12,13] After integration of eq 1, $\ln(C_{MeHg})_t$ could be simulated by $\ln(C_{MeHg})_0$ and cumulative PAR photon flux ($J$), as described in eq 2. The rate constant of MeHg degradation (with respect to photo flux), $k_D$, was then obtained by linear regression of $\ln(C_{MeHg})_t$ on $J$, using Origin (Version 6.0 for Windows, OriginLab Corp., Northampton, MA). The linear regression ($r^2$) and probability ($p$) were employed to evaluate the quality of the fit (see SI Figure S6). A previously proposed method was adopted to adjust the attenuation of solar radiation by Teflon bottles.[13] Values of $k_D$ obtained with Teflon bottles were amended using the literature reported transmittance of Ultraviolet (UV)-B (66%) and UV-A (82%) through Teflon bottles.[45]

$$\frac{dC_{MeHg}}{dt} = -k_D \times C_{MeHg} \times \text{PAR} \tag{1}$$

$$\ln(C_{MeHg})_t = \ln(C_{MeHg})_0 - k_D \times J \tag{2}$$

where $C_{MeHg}$ is the concentration of MeHg (ng L^{−1}); $k_D$ is the rate constant of MeHg photodegradation (m[2] E[−1]); PAR is the photosynthetically active radiation (E m^{−2} d^{−1}); and $J$ is cumulative PAR photon flux (E m^{−2}).

## ■ RESULTS AND DISCUSSION

**Effects of MeHg−DOM Complexation on MeHg Photodegradation.** Concentrations of Me[201]Hg decreased quickly in >3000 Da DOM solution (HWM), with a degradation rate constant of 17.6 ± 1.1 E[−1] m[2] (all presented as means ± standard deviation), significantly higher ($t$ test, $p <$ 0.01) than that in the unaltered Everglades water (12.0 ± 2.3 E[−1] m[2], Figure 1a). As concentrations of inorganic ions, such as Fe, Mn, $NO_3^-$, and $NO_2^-$, in the concentrated HWM DOM solutions were decreased to ∼10[−2]−10[−3] times the original concentrations (SI Table S1), DOM present in the solution was likely the determining factor for the photodegradation of MeHg in HWM solution. Rapid degradation of MeHg was also observed in LWM (21.1 ± 2.3 E[−1] m[2]) solution. The similar degradation rate constants in HWM and LWM suggested that both >3000 Da DOM and <3000 Da DOM could play an important role in MeHg photodegradation. Since the ion concentrations in LWM fraction were much higher than that in
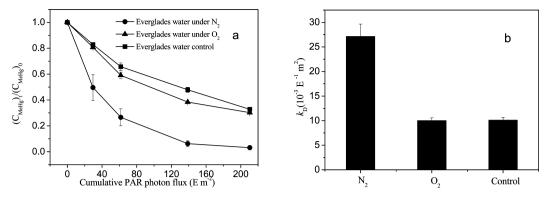
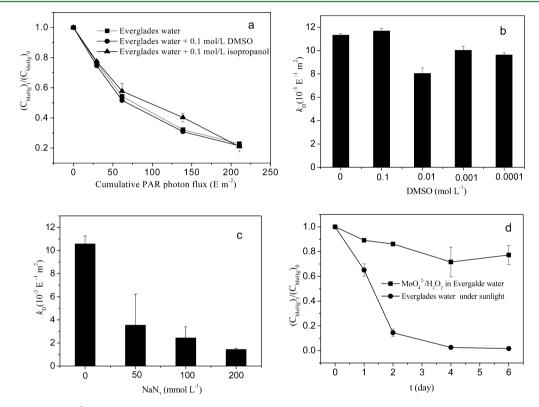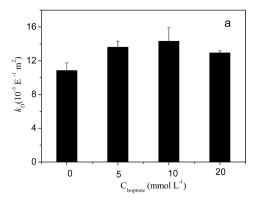**Figure 2.** Influence of purging with $N_2$ or $O_2$ on the photodegradation of MeHg in Everglades water.



**Figure 3.** Effects of ·OH and $^1O_2$ on MeHg photodegradation in Everglades water. (a) MeHg photodegradation in Everglades water with and without the addition of 100 mmol $L^{-1}$ isopropanol and DMSO, (b) MeHg photodegradation rate constants in Everglades water with various concentrations of DMSO, (c) MeHg photodegradation rate constants in Everglades water with various concentrations of $NaN_3$, (d) MeHg photodegradation in Everglades water in the absence and presence of $^1O_2$ generated from $MoO_4^{2-}/H_2O_2$ system.

HMW fraction, the similar photodegradation rate constants in both fractions also indicate that various ions may not be the driving factors for MeHg photodegradation in Everglades surface water. During the 6-days of incubation, the bacterial populations may be changed. However, our previous study[13] has demonstrated that the biotic degradation of MeHg does not play a significant role in MeHg degradation in Everglades surface waters. Thus, the changes in bacterial populations are not expected to affect the degradation of MeHg.

The importance of MeHg−DOM complexes in MeHg photodegradation was further examined by adding various competing ligands (CYS and DTT) in DI water and Everglades water. An appropriate competing ligand should have strong capacity of complexing MeHg, while at the same time does not directly photodegrade MeHg. Otherwise, it is impossible to differentiate the degradation of MeHg initiated by the

competing ligands or by DOM. Consistent with most previous studies,[19,20] MeHg cannot be degraded in DI water (control) under ambient solar radiation (Figure 1b, SI Figure S2). Concentration of MeHg was observed to be quickly decreased in CYS solution, with a photodegradation rate constant of 8.50 ± 3.4 $E^{-1}$ $m^2$ (Figure 1b). No significant degradation of MeHg was observed in the DI water containing DTT (*t* test, $p > 0.1$). These results suggested that DTT is an appropriate ligand for studying the importance of MeHg−DOM complexation.

In incubations without the addition of competing ligands, more than 97% of MeHg was calculated to be present in the form of MeHg−DOM without the addition of competing ligands, while this ratio decreased to approximately 0% in the presence of DTT (see SI for calculations). The reduction in MeHg photodegradation rate constant could have been caused by the decomposition of MeHg−DOM complexes, suggesting
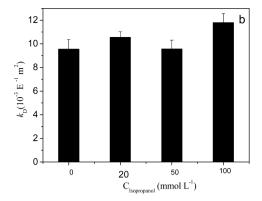
**Figure 4.** Effects of $^3DOM^*$ and $e^-_{aq}$ scavengers on MeHg photodegradation in Everglades water. (a) MeHg photodegradation rate constants in Everglades water with various concentrations of isoprene (scavenger of $^3DOM^*$), (b) MeHg photodegradation in $N_2O$-saturated Everglades water with various concentrations of isopropanol (scavenger of $e^-_{aq}$).

that DOM was likely involved in MeHg photodegradation by forming MeHg−DOM complexes in Everglades water. However, the addition of the competing ligands may also affect other parameters or processes that are involved in MeHg photodegradation, such as ionic strength, free radicals/reactive oxygen species, or bind with other metals (e.g., $Fe^{3+}$). In addition, the photodegradation of MeHg−DOM complexes may also be driven by free radicals/reactive oxygen species (pathway 2) (e.g., organic radicals, $\cdot OH$ and $^1O_2$)[17,19] according to the three possible mechanisms of MeHg photodegradation. MeHg photodegradation rate constants did not show significant difference (1-way ANOVA, $p > 0.1$) under multiple concentrations of NaCl (0−1 mol $L^{-1}$) in Everglades water (SI Figure S2), indicating that the changes in ionic strength after adding various competing ligands should not have a great impact on MeHg photodegradation. Effects of various free radicals/reactive oxygen species, including $\cdot OH$, $^1O_2$, $^3DOM^*$, $e^-_{aq}$, and organic radicals, were further studied to determine if these free radicals/reactive oxygen species were involved in the photodegradation of MeHg in Everglades water.

**Effects of Free Radicals/Reactive Oxygen Species ($\cdot OH$ and $^1O_2$) on MeHg Photodegradation.** The rate constants of MeHg photodegradation ($k_D$) in unaltered Everglades water (control) and in Everglades water purged with $O_2$ or $N_2$ were measured. The photodegradation rate constant under $N_2$ treatment ($27.15 \pm 2.50$ E$^{-1}$ m$^2$) was about three times larger than that of the control ($10.13 \pm 0.56$ E$^{-1}$ m$^2$) and $O_2$ treatment ($10.02 \pm 0.56$ E$^{-1}$ m$^2$) (Figure 2a and b). As the production of free radicals/reactive oxygen species is expected to increase under oxic conditions and decrease under anoxic conditions,[34,35] these results indicate that free radicals/reactive oxygen species may not play an important role in MeHg photodegradation in Everglades water. As this critical factor was often omitted in previous studies, the conclusion that free radicals/reactive oxygen species are the dominant factor[19,20] may need further verification. Purging the solutions with $N_2$ may also cause the loss of elemental mercury (assuming $Hg^0$ is the product) in solution and consequently affect the equilibrium of MeHg/Hg(II)/$Hg^0$. However, we observed that photodegradation of MeHg showed no difference for trials with or without purging with $O_2$ (at a same flow rate as $N_2$) ($t$ test, $p > 0.1$), indicating that the increase in $k_D$ should not be attributed to the loss of $Hg^0$ in solutions. The significant enhancement of MeHg photodegradation in treatment excluding $O_2$ implies that $O_2$ may serve as a scavenger of some intermediates of this process. To validate this finding,

scavenger addition experiments were conducted to investigate the effects of $\cdot OH$ and $^1O_2$ on MeHg photodegradation.

There were no significant differences between degradation of MeHg in the presence and absence of 0.1 mol $L^{-1}$ DMSO or isopropanol ($\cdot OH$ scavenger) ($t$ test, $p > 0.1$), downplaying the role played by $\cdot OH$ in MeHg photodegradation (Figure 3a). To exclude the possible effects of scavenger concentration, multiple concentrations of DMSO, ranging from $10^{-4}-10^{-1}$ mol $L^{-1}$, on MeHg photodegradation, were also examined (Figure 3b). Although 1-way ANOVA analysis showed that there were significant differences among the various levels of DMSO ($p < 0.01$), the photodegradation rate constant in the presence of DMSO was comparable to that in the nonspiking water (73−103%). This result supported our conclusion that $\cdot OH$ could not be the driver of MeHg photodegradation in Everglades water. The MeHg photodegradation rate constant significantly decreased (1-way ANOVA, $p < 0.01$) for the treatment with 50−200 mmol $L^{-1}$ $NaN_3$, an $^1O_2$ scavenger (Figure 3c). This result was inconsistent with the results of $N_2/O_2$ purge experiments which showed that reactive oxygen species were not involved in MeHg photodegradation. To confirm the role of $^1O_2$ in the photodegradation of MeHg, the degradation of MeHg in Everglades waters with $^1O_2$ generator, $MoO_4^{2-}/H_2O_2$ was compared with that under solar radiation (Figure 3d). Concentrations of $^1O_2$ in Everglades water with addition of $MoO_4^{2-}/H_2O_2$ ($10^{-11}$ mol $L^{-1}$, SI Table S6) was estimated to be approximately 100 times higher than that in Everglades water under solar radiation ($10^{-13}$ mol $L^{-1}$, SI Table S6). Therefore, the MeHg degradation rate constant in $MoO_4^{2-}/H_2O_2$ system was expected to be much higher than that under solar radiation if $^1O_2$ drives MeHg photodegradation. However, the experiments showed that MeHg degradation rate constant in $MoO_4^{2-}/H_2O_2$ (Figure 3d) was very slow (approximately 10% of that in Everglades water under solar radiation), indicating that $^1O_2$ should not be a primary driver of MeHg photodegradation. Thus, the decrease in MeHg photodegradation rate constants in the presence of $NaN_3$ is unlikely caused by the scavenging of $^1O_2$. As $N_3^-$ has a mild affinity for mercury, with a log $K_{Hg-DOM}$ of 7.74,[46] this decrease could be caused by the competition of $N_3^-$ with DOM for complexing MeHg. We then conducted experiments to measure the percentage of MeHg complexed with DOM in the absence and presence of $NaN_3$ (100 mmol $L^{-1}$) (SI Figure S3), using both dialysis bag and centrifuge-ultrafiltration. The results showed that MeHg complexed with DOM was dramatically decreased in the presence of $NaN_3$. This finding suggested that

NaN$_3$ can also serve as a competing ligand of DOM for complexing with MeHg. This result indicates that the previous conclusion that $^1O_2$ drives MeHg photodegradation[19] does not fit the environments that MeHg–DOM complexes are involved in this process, as the adopted scavenger of $^1O_2$ (NaN$_3$) can inhibit MeHg photodegradation by both scavenging $^1O_2$ and competing with DOM for complexing with MeHg.

**Effects of $^3$DOM*, e$^-_{aq}$ and Organic Radicals on MeHg Photodegradation.** In our current study, free radicals/reactive oxygen species were found to play a minor role in the photodegradation of MeHg in Everglades water. In addition to ·OH and $^1O_2$, e$^-_{aq}$,[28−30] $^3$DOM*,[26,27] can also exist in the aquatic environments and be involved in the photodegradation of different pollutants in water. $^3$DOM*, a strong oxidant with the effective one-electron reduction potential of at least 1.36 V, can be involved in photochemical processes in natural waters through direct reaction with pollutants or by sensitizing O$_2$ to $^1O_2$.[47] As one of the strongest reducing agent with an effective one-electron reduction potential of −2.84 V, e$^-_{aq}$ can be produced from sunlit DOM and has been proven to play an important role in the phototransformation of hydrophobic halogenated aromatic hydrocarbons.[48,49] In addition, $^3$DOM* and e$^-_{aq}$ prefer anoxic conditions.[50] If MeHg photodegradation was driven by either of them, the increase in MeHg photodegradation rate constants under anoxic conditions could be explained.

The role of $^3$DOM* in MeHg photodegradation was examined by adding isoprene as the scavenger for $^3$DOM* (Figure 4a). The MeHg photodegradation rate constants did not decrease with the addition of isoprene (0–20 mmol L$^{-1}$). N$_2$O/isopropanol was chosen as the scavenging system for e$^-_{aq}$. In the N$_2$O saturated Everglades water, the photodegradation of MeHg showed no significant difference (1-way ANOVA, $p >$ 0.1) for the trials with or without the addition of isopropanol (0−100 mmol L$^{-1}$) (Figure 4b). These results indicate that both e$^-_{aq}$ and $^3$DOM* are not the major reactive species inducing the photodegradation of MeHg.

The role of organic radicals on MeHg photodegradation was evaluated by diluting Everglades water (Figure 5). Previous
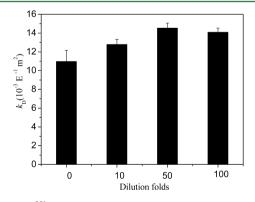


**Figure 5.** Me$^{201}$Hg photodegradation rate constants in Everglades waters and diluted Everglades water (diluted 10, 50, and 100 folds).

studies on the transformation of Fe (II)/Fe(III), Cr(VI)/Cr(III) and Hg(II)/Hg$^0$ induced by organic radicals showed that the transformation rate was dependent on the concentration of organic matter.[51−53] The results in this study show that the photodegradation rate of MeHg did not decrease with increasing dilution of Everglades water DOM (up to 100 times), indicating that organic radicals may not be the

intermediates driving MeHg photodegradation. However, it should be noted that diluting a natural water sample can change both the production and consumption rates of organic radicals. If the reaction orders were similar for both production and consumption reactions, the decrease in both processes would be similar, resulting in a comparable amount of organic radicals in the diluted waters. In water, DOM can absorb most UV radiation over a very short path length. The slightly increased $k_D$ in diluted surface water could be attributed to the decreased concentrations of DOM.

Our data suggests that the role of free radicals/reactive oxygen species in photodegradation of MeHg in Everglades water is minimal. The decrease in MeHg photodegradation rates with the addition of competing ligands is expected to be caused by the decomposition of MeHg–DOM complexes, rather than their effect on the factors that determine the production of free radicals/reactive oxygen species. By integrating all results obtained in this study and others, a mechanism involving direct photodegradation of MeHg–DOM complexes via intramolecular charge transfer is proposed as the pathway of MeHg photodegradation in Everglades surface water. The proposed photodegradation of MeHg involves two steps: the excitation of MeHg–DOM complexes under solar radiation, and the subsequent degradation of MeHg–DOM complexes at an exited state (reactions 1 and 2). The O$_2$ could deactivate (MeHg−DOM)* (reaction 3), thus inhibiting the photodegradation of MeHg. Although little is known about the possibility of direct photodegradation of MeHg−DOM complexes, direct transfer of electrons from photosensitized DOM to Hg$^{2+}$ within Hg$^{2+}$−DOM complexes have been proposed as a possible pathways for Hg$^{2+}$ photoreduction.[54] DOM contains abundant electron-donating functional groups, such as hydroquinones or semiquinones,[55,56] which can reduce various metal ions, for example, Hg$^{2+}$[57] and Fe$^{3+}$.[58] Based on the results of this study, we hypothesize that direct photodegradation of MeHg−DOM complexes via MeHg−DOM charge transfer may be the dominant pathway of MeHg photodegradation in Everglades water.

$$MeHg - DOM \xrightarrow{h\nu} (MeHg - DOM)^* \tag{1}$$

$$(MeHg - DOM)^*$$
$$\rightarrow MeHg \text{ degradation products} + DOM \tag{2}$$

$$(MeHg - DOM)^* + O_2 \rightarrow (MeHg - DOM) + {}^1O_2 \tag{3}$$

Pathways of MeHg photodegradation varied in different aquatic ecosystems, as evidenced by inconsistent results reported in this study and previous studies.[18] The variation of MeHg photodegradation pathway in different aquatic systems may be caused by differences in water chemistry, for example, concentration and chemical characteristics of DOM. For example, the ratio of Fe/DOC (dissolved organic carbon) in an Arctic lake[20] was approximately 20 times larger than that in Everglades, which may cause the different pathways of MeHg photodegradation in these two systems. A recent study showed that the mass independent fractionation (MIF) of MeHg by photodemethylation was significantly affected by the amount of reduced organic sulfur,[59] implying that concentrations and characterization of DOM may also play an important role in determining the dominant pathway of MeHg photodegradation in natural water. In this study, MeHg was observed to be

relatively stable in $NaN_3$ solution and it can be quickly degraded in cysteine solution. This may be due to the variation of $\Delta E_{S\text{-}T}$ in these MeHg complexes. Theoretical calculations indicate that $\Delta E_{S\text{-}T}$ of MeHg−OH, and MeHg−Cl (pathway 1) ($\Delta E_{S\text{-}T}$ 5.1−5.9 eV[22]) was higher than the high energy limit of the solar spectrum (4.4 eV[23]). However, $\Delta E_{S\text{-}T}$ of MeHg in the form of MeHg-organic sulfur compound could be decreased to 3.6 eV,[60] making the direct degradation of MeHg-organic sulfur compound by solar radiation feasible. More reduced sulfur-containing compounds can be formed in anoxic conditions to bind MeHg. If thiol was the functional group dominating MeHg photodegradation, it could explain the higher photodegradation rates under anoxic conditions. In fact, several previous studies[17,19] have provided experimental evidences on the possible importance of MeHg-SR (thiol) interactions in DOM for the photodegradation of MeHg. Future work should be conducted to validate which functional groups in DOM dominate the MeHg photodegradation. Due to the differences in water chemistry in aquatic systems, for example, concentration levels of DOM, $Fe^{3+}$, $NO_3^-$, comparative studies on several systems with significant differences in aquatic chemistry (e.g., marine, wetland, and lake waters) should be conducted to determine the factors controlling the variation in the pathways of MeHg photodegradation.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org

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### Notes
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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