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Photochemical Oxidation of Dissolved Elemental Mercury by Carbonate Radicals in Water

Feng He,^{*,†,§} Weirong Zhao,[‡] Liyuan Liang,[†] and Baohua Gu^{*,†}

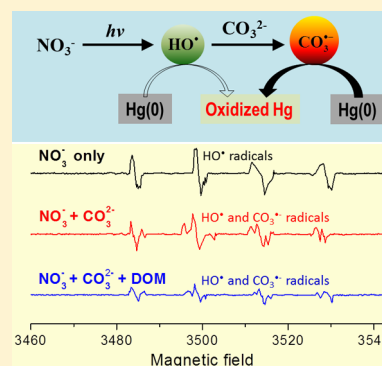
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S Supporting Information

ABSTRACT: Photochemical oxidation of dissolved elemental mercury, Hg(0), affects mercury chemical speciation and its transfer at the water–air interface in the aquatic environment. The mechanisms and factors that control Hg(0) photooxidation, however, are not completely understood, especially concerning the role of dissolved organic matter (DOM) and carbonate (CO_3^{2-}) in natural freshwaters. Here, we evaluate Hg(0) photooxidation rates affected by reactive ionic species (e.g., DOM, CO_3^{2-} , and NO_3^-) and free radicals in creek water and a phosphate buffer solution (pH 8) under simulated solar irradiation. The Hg(0) photooxidation rate ($k = 1.44 \text{ h}^{-1}$) is much higher in the presence of both CO_3^{2-} and NO_3^- than in the presence of CO_3^{2-} , NO_3^- , or DOM alone ($k = 0.1\text{--}0.17 \text{ h}^{-1}$). Using scavengers and enhancers for singlet oxygen ($^1\text{O}_2$) and hydroxyl (HO^\bullet) radicals, as well as electron paramagnetic resonance spectroscopy, we found that carbonate radicals ($\text{CO}_3^{\bullet-}$) primarily drive Hg(0) photooxidation. The addition of DOM to the solution of CO_3^{2-} and NO_3^- decreased the oxidation rate by half. This study identifies an unrecognized pathway of Hg(0) photooxidation by $\text{CO}_3^{\bullet-}$ radicals and the inhibitory effect of DOM, which could be important in assessing Hg transformation and the fate of Hg in water containing carbonate such as hard water and seawater.



INTRODUCTION

Photochemical reduction and oxidation of mercury (Hg) are important for determining Hg chemical speciation, bioaccumulation, and geochemical cycling in aquatic environments.^{1–9} While the photoreduction of Hg(II) has been extensively studied,^{3–6,9–11} only a few studies have focused on the photooxidation of Hg(0) in aquatic systems,^{1,2,12–14} and mechanisms by which Hg(0) is oxidized remain unclear. Hg(0) is known to exist in terrestrial water bodies and the ocean.^{3,15,16} In contaminated creeks, high Hg(0) concentrations (0.3–8 ng/L) have been observed.¹⁷ Previous studies have shown that Hg(0) can be rapidly oxidized in seawater or freshwater salted with 500 mM chloride (Cl^-) under light or dark conditions, but little oxidation occurred when a small amount of salt (0.5 mM Cl^-) was added to the freshwater.^{3,14} It is hypothesized that Cl^- stabilized the oxidative products [by forming Hg(II)Cl_n^{2-n} species], thereby facilitating oxidation. Similarly, Lalonde et al.¹ demonstrated in the laboratory that photooxidation of Hg(0) required the simultaneous presence of Cl^- and a photoreactive compound (*p*-benzoquinone). They hypothesized that the role of Cl^- may be to stabilize Hg(I) ions in solution, thereby decreasing the reduction potential of the Hg(I)/Hg(0) couple and facilitating the transfer of an electron to the benzoquinone. However, when benzoquinone was replaced with naturally dissolved organic matter (DOM), little Hg(0) oxidation occurred. Furthermore, they found significant photooxidation of Hg(0) in natural freshwaters without the

addition of Cl^- , which was contrary to what was observed in the laboratory. They speculated that either enough Cl^- is present in the freshwater or some inorganic or organic ligand effectively formed complexes with Hg(I) leading to Hg(0) photooxidation. In a subsequent study, these authors reported that addition of methanol, a hydroxyl radical (HO^\bullet) scavenger, decreased the Hg(0) photooxidation rate by 25% in the brackish water from the St. Lawrence River and by 19% in an artificial saline containing *p*-benzoquinone.¹⁸ They concluded that HO^\bullet radicals may be partially responsible, although direct evidence of their involvement in Hg(0) photooxidation is lacking. It is also unclear what other reactive oxygen species (ROS) may be involved in the reaction.

Photolysis of natural water can generate many types of ROS, including HO^\bullet , singlet oxygen ($^1\text{O}_2$), superoxide radicals ($\text{O}_2^{\bullet-}$), and DOM-derived oxyl and peroxy radicals (RO^\bullet and ROO^\bullet),^{19–22} although $\text{O}_2^{\bullet-}$ is ineffective in oxidizing Hg(0) because of its relatively low oxidation potential.¹⁸ Hydroxyl radicals are among the most reactive and commonly observed in natural water through direct photolysis of, for example, nitrate (NO_3^-), H_2O_2 , and DOM, as well as through Fenton-type reactions.^{19–21} Additionally, secondary radicals

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such as carbonate ($\text{CO}_3^{\bullet-}$) can form via reactions between HO^\bullet and CO_3^{2-} ions and have been shown to oxidize certain aromatic and sulfur-containing organic compounds.^{22–24} Although its relative abundance and ability to oxidize $\text{Hg}(0)$ have not been demonstrated in natural waters, $\text{CO}_3^{\bullet-}$ has a standard potential of 1.6 V, sufficiently high to oxidize $\text{Hg}(0)$.¹⁹ Natural hard waters and seawater usually contain millimolar concentrations of dissolved carbonate species (CO_3^{2-} , HCO_3^- , and H_2CO_3), and we thus hypothesize that $\text{CO}_3^{\bullet-}$ may have played a role in causing $\text{Hg}(0)$ photooxidation. We aimed to determine if the photooxidation of $\text{Hg}(0)$ is predominantly induced by $\text{CO}_3^{\bullet-}$, HO^\bullet , or $^1\text{O}_2$ radicals in water and what roles CO_3^{2-} , NO_3^- , DOM, and Fe(III) played in these reactions.

MATERIALS AND METHODS

Freshwater samples were collected in 1 L Teflon bottles (without headspace) at a depth of 0.5 m from the Hg-contaminated East Fork Poplar Creek (EFPC) in Oak Ridge, TN, ~21.5 km from the headwater.¹⁷ Samples were filtered through 0.45 μm membrane filters in the laboratory, purged with purified gas (Zero air, Air Liquide) until no purgeable gaseous $\text{Hg}(0)$ was detected, and stored in the refrigerator (4 $^\circ\text{C}$) until use. The filtered samples were analyzed for major cations by an inductively coupled plasma mass spectrometer (PerkinElmer) and anions by ion chromatography (Dionex).²⁵ The water contained 2 pM $\text{Hg}(0)$ and 0.13 nM $\text{Hg}(\text{II})$. The DOM concentration was 0.16 mM (as C), and the total carbonate concentration was 2.75 mM (as dissolved inorganic C). The NO_3^- , Cl^- , and SO_4^{2-} concentrations were 0.23, 0.35, and 0.21 mM, respectively. The pH was ~8, and the dissolved oxygen concentration was 0.28 mM.

The dissolved $\text{Hg}(0)$ stock solution was prepared, and its purity and concentration were determined following previously established procedures.^{26–28} Typically, the stock solution consisted of 150–200 nM $\text{Hg}(0)$ and <1.6 nM $\text{Hg}(\text{II})$. The creek water (45 mL) was then mixed with varying amounts of the $\text{Hg}(0)$ stock in an anaerobic glove chamber (Coy) to reach a volume of 60 mL, and final $\text{Hg}(0)$ concentrations were in the range of 0.7–30 nM. Samples were immediately transferred to a large plastic syringe (without headspace) and subsequently dispensed into a series of 6 mL acid-cleaned quartz vials, capped without any headspace.

The photooxidation experiment was begun by placing the sample vials in a simulated solar chamber (Suntest XLS+, Atlas) equipped with a 300 nm wavelength cutoff daylight filter (spectrum reported previously).²⁹ The light irradiance was 40 W m^{-2} for UV (300–400 nm) and ~373.6 W m^{-2} total (300–800 nm), typical of midsummer conditions in eastern Tennessee.^{29,30} The reaction temperature was kept at 30 ± 1 $^\circ\text{C}$. Dark controls were performed in the same manner in vials wrapped with aluminum foil. At selected time intervals, an aliquot (0.5 mL) was taken from sacrificial sample vials and transferred to a 3 mL amber glass vial, which was immediately sealed and analyzed for purgeable $\text{Hg}(0)$, as described previously.^{26–28} The amount of nonpurgeable Hg remaining was determined by first oxidizing the sample in BrCl [5% v/v] overnight and then analyzing total Hg concentrations.^{31,32}

Parallel experiments were performed to examine the roles of $^1\text{O}_2$ and $^\bullet\text{OH}$ free radicals in $\text{Hg}(0)$ photooxidation using 2-propanol [0.1% v/v] as a $^\bullet\text{OH}$ inhibitor and sodium azide (NaN_3 , 10 mM) as an inhibitor for both $^1\text{O}_2$ and $^\bullet\text{OH}$ radicals.^{29,33} Separately, heavy water (D_2O) was used as a $^1\text{O}_2$

enhancer in $\text{Hg}(0)$ photooxidation.^{33,34} To determine the roles of reactive ionic species such as NO_3^- , CO_3^{2-} , DOM, and Fe(III) in $\text{Hg}(0)$ photooxidation, similar experiments were performed by adding each or a combination of the ionic species to a phosphate-buffered solution (PBS), consisting of 0.9 mM NaH_2PO_4 , 19.8 mM Na_2HPO_4 , and 0.35 mM NaCl at pH 8.0 \pm 0.1. Carbonate was added as NaHCO_3 , and the DOM was isolated from EFPC, as described previously.^{29,35}

Electron paramagnetic resonance (EPR) spin trapping analysis using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was performed to directly probe the generation and abundance of photochemically produced $^\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ radicals.^{36,37} Samples containing NO_3^- alone, a mixture of NO_3^- and CO_3^{2-} , and a mixture NO_3^- , CO_3^{2-} , and DOM were prepared in PBS in the same manner, except higher concentrations of NaNO_3 (8.3 mM), NaHCO_3 (100 mM), and DOM (8.3 mM C) were used than in the photochemical experiments because of the low sensitivity of the EPR technique. DMPO was added to each sample to give a final concentration of 50 mM, and radicals were generated by irradiating samples with a UV lamp (254 nm) at room temperature. EPR spectra were recorded for 10 min using a Bruker ESRA-300 spectrometer with a microwave power of 20.25 mW at the working frequency of 9.86 GHz and a modulation amplitude of 1 G at 100 kHz.

RESULTS AND DISCUSSION

In the EFPC water, the spiked $\text{Hg}(0)$ (at 20 nM) rapidly photooxidized with an estimated first-order rate constant of 0.61 h^{-1} (Figure 1a). The rate did not change significantly with initial $\text{Hg}(0)$ concentrations from 0.7 to 30 nM (Table S1 of the Supporting Information), probably because of a large excess of the reactive ionic species relative to $\text{Hg}(0)$ in the EFPC water. However, in the dark or in the absence of reactive ionic species, i.e., reactions in either deionized water or PBS, no $\text{Hg}(0)$ photooxidation occurred (Figure 1). These results clearly show that $\text{Hg}(0)$ oxidation is photochemically induced, and certain ionic species or intermediates in the creek water caused $\text{Hg}(0)$ photooxidation. The rate observed in EFPC (0.61 h^{-1}) was similar to those (0.54–0.87 h^{-1}) observed in saline and brackish water,^{1,18} in which high Cl^- concentrations (>500 mM) were thought to be responsible. At low Cl^- concentrations (0.35 mM in PBS), no $\text{Hg}(0)$ photooxidation was observed either (Figure 1b), suggesting that reactive species, other than Cl^- , in the creek water must be driving the photooxidation of $\text{Hg}(0)$.

We subsequently evaluated the contribution of each or a combination of the following ionic species to $\text{Hg}(0)$ photooxidation in PBS. They include (1) DOM (0.16 mM C), (2) DOM and Fe(III) (as FeCl_3 at 1.5 μM), (3) NO_3^- alone (0.23 mM), (4) a mixture of NO_3^- (0.23 mM) and CO_3^{2-} (as NaHCO_3 at 2.75 mM), and (5) a mixture of DOM, NO_3^- , and CO_3^{2-} . With DOM alone, we found little or no increased $\text{Hg}(0)$ photooxidation (Figure 1b), and the rate constant was 0.1 h^{-1} (Table S1 of the Supporting Information), suggesting that DOM was not a major factor in causing $\text{Hg}(0)$ photooxidation. The addition of Fe(III) to the DOM solution only slightly increased the oxidation rate ($k = 0.14$ h^{-1}); thus, the Fenton-type reaction was not a major mechanism either.³⁸ Nitrate appeared to be more effective than DOM, with a rate constant of 0.17 h^{-1} . However, the rates observed in the presence of NO_3^- or DOM or their combinations are still much lower than that observed in the EFPC water [$k = 0.61$ h^{-1} (Figure 1a)].

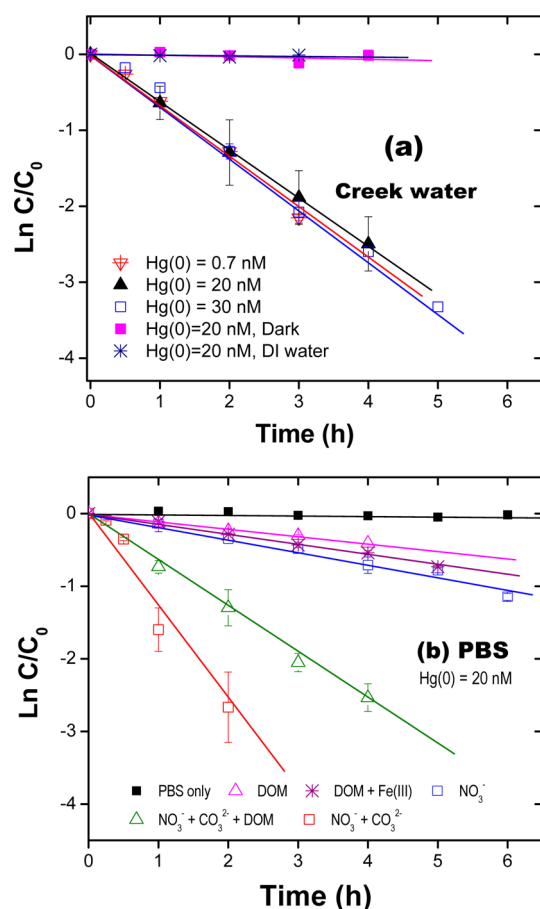


Figure 1. (a) Natural logarithmic plots of Hg(0) photooxidation in EFPC creek water (pH ~ 8) spiked with dissolved Hg(0) at initial concentrations (C_0) of 0.7, 20, and 30 nM under simulated solar irradiation. The dark control was performed in quartz vials wrapped with aluminum foils. (b) Photooxidation of Hg(0) ($C_0 = 20$ nM) in PBS (pH 8) amended separately with DOM, DOM and Fe(III), NO_3^- , NO_3^- and CO_3^{2-} , or NO_3^- , CO_3^{2-} , and DOM. The error bars represent one standard deviation from two to four batch measurements.

Only when both NO_3^- and CO_3^{2-} were present was a substantially increased photooxidation rate (1.44 h^{-1}) observed (Figure 1b). This rate is ~ 8 -fold higher than that observed in the presence of NO_3^- alone, indicating that carbonate may be the major species responsible for enhancing Hg(0) photooxidation. However, addition of DOM to the solution described above (NO_3^- and CO_3^{2-}) decreased the Hg(0) photooxidation rate by half (0.71 h^{-1}), although this rate is still 4–5 times higher than that in the presence of either NO_3^- or DOM alone. Importantly, the rate (0.71 h^{-1}) in the presence of multiple species of NO_3^- , CO_3^{2-} , and DOM was nearly identical to that observed in EFPC water ($0.61\text{--}0.72 \text{ h}^{-1}$) (Table S1 of the Supporting Information), suggesting that these ionic species likely control Hg(0) photooxidation in EFPC. Although DOM alone increased the Hg(0) photooxidation rate compared with the control (Figure 1b), in water with multiple species it acted as a net sink, rather than a source of HO^\bullet radicals, and decreased the Hg(0) photooxidation rate. Previous studies also showed that DOM can act as an effective quencher of HO^\bullet radicals.^{19,22}

Nitrate is known to photochemically produce HO^\bullet and has been considered as the major contributor of ROS in natural

water.^{21,39} The NO_3^- concentration in EFPC is $\sim 0.23 \text{ mM}$, but NO_3^- alone only moderately increased the Hg(0) photooxidation rate (0.17 h^{-1}). Thus, the amount of HO^\bullet produced from NO_3^- was either insufficient for Hg(0) oxidation or rapidly scavenged in the water. On the basis of a reported rate constant of $(2.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for reactions between HO^\bullet and Hg(0),^{19,21} a steady state HO^\bullet concentration of $\sim 7.0 \times 10^{-14} \text{ M}$ is required to sustain a Hg(0) photooxidation rate of 0.61 h^{-1} . This HO^\bullet concentration is at least 1 order magnitude higher than that typically observed in surface water ($10^{-16}\text{--}10^{-15} \text{ M}$)^{19,21} because of the high reactivity of HO^\bullet with many natural scavengers. HO^\bullet may be produced via other processes such as direct photolysis of DOM and Fenton-type reactions involving Fe(III),^{20,21} but our results show that DOM or a mixture of DOM and Fe(III) did not lead to an appreciably increased Hg(0) photooxidation rate (Figure 1b).

Studies, however, have shown that HO^\bullet can react with carbonate to yield relatively long-lived $\text{CO}_3^{\bullet-}$ radicals,^{19,22} particularly at systems like EFPC above neutral pH. Carbonate radicals are less reactive than HO^\bullet radicals, leading to slower reactions with natural scavengers.⁴⁰ As a result, the $\text{CO}_3^{\bullet-}$ steady state concentration can reach as high as $10^{-15}\text{--}10^{-13} \text{ M}$, nearly 2 orders of magnitude higher than that of HO^\bullet in surface water.¹⁹ The addition of NO_3^- and CO_3^{2-} together has led to a substantially increased Hg(0) photooxidation rate (Figure 1b), implying that HO^\bullet radicals that formed from the photolysis of NO_3^- reacted with CO_3^{2-} to form $\text{CO}_3^{\bullet-}$ radicals, which then oxidized Hg(0). Because carbonate alone does not photochemically produce $\text{CO}_3^{\bullet-}$ or HO^\bullet ,^{19,36} we conclude that $\text{CO}_3^{\bullet-}$ radicals are formed via a secondary process and are the primary radicals for the photooxidation of Hg(0).

We further evaluated the role of $^1\text{O}_2$ and HO^\bullet in Hg(0) photooxidation using 2-propanol as a HO^\bullet scavenger and NaN_3 as a scavenger for both $^1\text{O}_2$ and HO^\bullet , as described previously.^{29,33,34} Addition of 2-propanol decreased the Hg(0) photooxidation rate by 83%, whereas NaN_3 decreased the rate by 92% (Figure 2). These results confirm that HO^\bullet

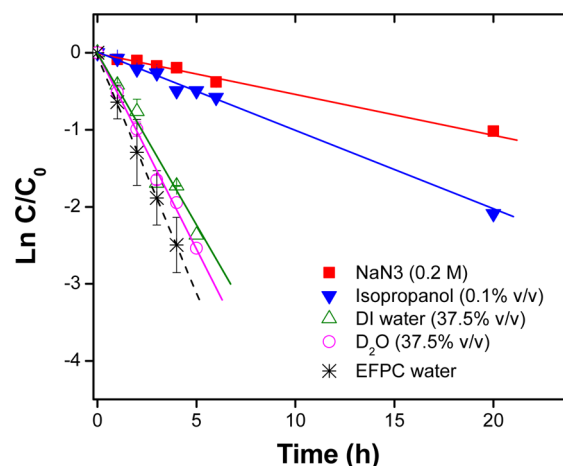


Figure 2. Natural logarithmic plots of Hg(0) photooxidation in EFPC creek water in the presence or absence of 2-propanol [0.1% (v/v)] as a HO^\bullet inhibitor and sodium azide (NaN_3 , 10 mM) as an inhibitor of both $^1\text{O}_2$ and HO^\bullet radicals.^{29,33} Deuterium water (D_2O) was used as a $^1\text{O}_2$ enhancer.^{33,34} Experiments were performed under simulated solar irradiation with an initial Hg(0) concentration (C_0) of 20 nM, and error bars represent one standard deviation from two to four batch measurements.

and/or $^1\text{O}_2$ radicals are involved in $\text{Hg}(0)$ photooxidation. NaN_3 was slightly more effective than 2-propanol in inhibiting $\text{Hg}(0)$ photooxidation because NaN_3 can scavenge both $^1\text{O}_2$ and HO^\bullet . To distinguish the roles of these two radicals, similar experiments were performed with either deuterated water (D_2O) (37.5%) or deionized H_2O (37.5% as a controls) added to EFPC water (62.5%). Because quenching $^1\text{O}_2$ is ~ 13 times slower in D_2O than in H_2O ,^{34,41} the use of D_2O would prolong the life of $^1\text{O}_2$ and thus increase the photooxidation rate if $^1\text{O}_2$ were the primary reactive intermediate. However, the rate decreased slightly for samples with either D_2O or H_2O added (Figure 2). The decreased $\text{Hg}(0)$ photooxidation rate is attributed to the dilution of ionic species originally present in EFPC by the addition of D_2O or H_2O . These observations further support the conclusion described above that HO^\bullet reacted with carbonate to form secondary $\text{CO}_3^{\bullet-}$ radicals, thereby driving the photooxidation of $\text{Hg}(0)$.

EPR spectroscopic measurements provided direct evidence of the formation of HO^\bullet and $\text{CO}_3^{\bullet-}$ radicals in samples containing (a) NO_3^- , (b) NO_3^- and CO_3^{2-} , and (c) NO_3^- , CO_3^{2-} , and DOM in PBS (Figure 3). The spectrum in Figure

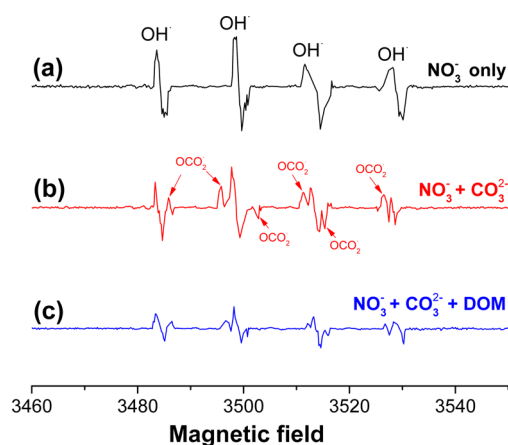


Figure 3. Electron paramagnetic resonance (EPR) spin-trap analysis of free radicals in PBS (pH 8) containing (a) NO_3^- , (b) NO_3^- and CO_3^{2-} , and (c) NO_3^- , CO_3^{2-} , and DOM. Spectra were acquired for 10 min, while irradiating samples under a UV lamp (254 nm), at a microwave power of 20.25 mW, a working frequency of 9.86 GHz, and a modulation amplitude of 1 G at 100 kHz. No signal was detected in control samples of CO_3^{2-} in PBS or PBS only (Figure S1 of the Supporting Information).

3a is characteristic of the DMPO-OH adduct with $g = 2.00693$ and has hyperfine splitting constant values (a_N and $a_{\beta\text{-H}}$) of 14.86 G, consistent with previous studies.^{37,42} It clearly showed the formation of HO^\bullet under UV irradiation in the presence of NO_3^- . In the absence of NO_3^- (i.e., CO_3^{2-} in PBS or PBS alone), no signal or free radicals were observed (Figure S1 of the Supporting Information). When both NO_3^- and CO_3^{2-} were present, we observed both DMPO-OH and DMPO-OCO_2 adducts (Figure 3b), with the latter showing $g = 2.00063$ and hyperfine splitting constants for $a_N = 14.35$ G, $a_{\beta\text{-H}} = 10.70$ G, and $a_{\gamma\text{-H}} = 1.38$ G.^{36,42} The spectrum also showed a decreased DMPO-OH signal intensity, indicating the trapping of HO^\bullet by carbonate to form $\text{CO}_3^{\bullet-}$ radicals. However, with the addition of DOM to a solution containing NO_3^- and CO_3^{2-} (Figure 3c), the same DMPO-OH and DMPO-OCO_2 adducts were detected, but their signal intensities both decreased, indicating the quenching effect of DOM. This result

is consistent with the observation that DOM decreased, rather than increased, $\text{Hg}(0)$ photooxidation rates (Figure 1b).

Taken together, our findings identify a new pathway for $\text{Hg}(0)$ photooxidation by $\text{CO}_3^{\bullet-}$ radicals in freshwater containing carbonate species. The photolysis of NO_3^- produces HO^\bullet , which reacts with CO_3^{2-} to form secondary $\text{CO}_3^{\bullet-}$ radicals (Table S2 of the Supporting Information). The $\text{CO}_3^{\bullet-}$ then reacts with $\text{Hg}(0)$ to form oxidized $^*\text{HgOH}$ species, which are subsequently oxidized by a variety of ROS to form $\text{Hg}(\text{OH})_2$, as reported previously.^{2,43} The latter reaction is fast with a rate constant on the order of $10^9\text{--}10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁴³ We note that HO^\bullet can also oxidize $\text{Hg}(0)$ to form $^*\text{HgOH}$,² but our results indicate that this reaction was not dominant in EFPC water. Additionally, photoreduction of $\text{Hg}(\text{II})$ to $\text{Hg}(0)$ is widely recognized in surface water and can occur concurrently with the photooxidation reactions.^{3–6} Thus, the measured concentrations of $\text{Hg}(\text{II})$ or $\text{Hg}(0)$ in these experiments reflect the net result of the two processes. Depending on the $\text{Hg}(0)$ to $\text{Hg}(\text{II})$ ratio and the ionic species (e.g., NO_3^- , CO_3^{2-} , and DOM), one process may dominate the other, thereby affecting Hg chemical speciation and $\text{Hg}(0)$ transfer at the water–air interface in surface water bodies and the ocean.^{9,10,44}

■ ASSOCIATED CONTENT

■ Supporting Information

Simulated solar light spectrum, rate constants, EPR analyses, and $\text{Hg}(0)$ photooxidation reactions. 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.

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