Photoinduced Oxidation of Hg^0(aq) in Waters from the St. Lawrence Estuary

J A N I C K D . L A L O N D E , M A R C A M Y O T , J O R D O R V O I N E , F R A N Ç O I S M . M . M O R E L , J E A N - C H R I S T I A N A U C L A I R , A N D P A R I S A A . A R I Y A

The oxidation of volatile aqueous Hg ^{0} in aquatic systems may be important in decreasing the fluxes of Hg out of the water column. Using incubations of natural samples from the St. Lawrence River, we examined some of the parameters that control this oxidation. Hg ^{0} was found to be chiefly mediated by UV radiation since (i) "dark" oxidation was not found to be statistically significant; (ii) visible light induced a significant but slow photooxidation (k= 0.09 h^{-1}); and (iii) visible + UV radiation led to a faster photooxidation (k $=$ 0.6– 0.7 h^{-1}), mainly because of UV-A induced reactions. Doubling UV irradiation did not increase the reaction rate of Hg^0 photooxidation in natural water samples, indicating that some factor other than photon flux was rate limiting and suggesting that the reaction involves intermediate photoproduced oxidant(s). The addition of methanol, a $^\bullet$OH scavenger, decreased Hg photooxidation rates by 25% in brackish waters and by 19% in artificial saline water containing semiquinones, indicating that $^\bullet$OH may be partly responsible for Hg^0 oxidation. Photooxidation rates were not affected by oxygen concentrations and did not decrease when samples were heat-sterilized, treated with chloroform, or filtered prior to exposure to light.

Introduction

Hg(II) reduction in natural waters produces volatile Hg ^{0}, which favors a water-to-air Hg transfer that reduces the Hg load in the system. The opposite reaction, Hg ^{0} oxidation, decreases the volatile Hg ^{0} pool and the water-to-air Hg transfer. Hg ^{0} oxidation could therefore increase the pool of Hg(II), which can be methylated and bioaccumulated in the aquatic food chain. Understanding the parameters that govern Hg ^{0} oxidation is therefore crucial to assess the potential for Hg ^{0} volatilization from a given aquatic system.

Hg^0 oxidation occurs heterogeneously on particle surfaces as well as in gaseous and aqueous phases. Numerous studies have shown that it occurs in laboratory gaseous phases (ref 1 and references therein) and in the oxidizing environment of the atmosphere ($2-7$). Fewer publications report oxidation of Hg^0 in laboratory solutions (8, 9) or in natural waters containing natural or low levels of Hg ^{0}(aq) ($10-13$).

In the field, Hg ^{0} oxidation has been reported in seawater (10, 12), in brackish water (11), and to a lesser extent in freshwater (k $=$0.1–0.3 h^{-1}) (11, $13-15$; Table 1). Reaction rates vary with sampling locations and seem to increase with chloride ion concentrations (10, 11; Table 1). This difference in oxidation rates between fresh and saline waters is consistent with more important Hg fluxes observed out of freshwater as com pared to seawater (16).

In addition to salinity, sunlight influences Hg ^{0} oxidation in natural waters. Dark oxidation was observed after an initial sunlight incubation in coastal waters (10) and in freshwater ($13-15$; Table 1) while oxidation was reported to occur after Hg(II) reduction when natural saline water was continuously exposed to sunlight (10, 11). These results suggest that Hg(II) reduction and Hg ^{0} oxidation occur simultaneously in natural waters and that we observe in the field the net result of these opposite processes. Lalonde et al. (11) increased the natural Hg^0(aq) levels to sub-nanomolar and observed a Hg ^{0} photo- oxidation in brackish waters incubated under a UV lam p simulating the sun's UV intensity but also emitting in the visible range (k $=$ 0.5–0.9 h^{-1} assuming a first-order kinetics). Clearly sunlight induces Hg ^{0} oxidation; however, the action spectrum of the reaction is unknown. The relative energy of the different solar wavelengths will influence the depth of penetration and the rate at which Hg ^{0} can be oxidized within the water column. Hg ^{0} oxidation would occur at shallower depths if induced by UV-B rather than by UV-A or visible light (17).

Although little is known about the oxidation mechanism in natural waters, laboratory experiments carried out under a variety of conditions can provide some insight. Hg ^{0} oxidation appears to be effected by organic acids such as semiquinones in artificial saline waters (11) and by organic acids in a variety of aqueous phases (18). The hydroxyl radical ($^\bullet$OH) considered to be one of the most reactive, photo- chemically produced free radical in the environment also appears to be an oxidant of Hg ^{0} in aqueous phase (16, $19- 21$). $^\bullet$OH can be produced in aqueous phases via photo- chemical and redox reactions involving superoxide and hydrogen peroxide. It is also produced in natural seawater through direct photolysis of NO $_3{}^-$, NO2$^-$, H2O2, and dissolved organic matter as well as through Fenton-type reactions (involving Fe(II) and H $_2$O2) (22). The superoxide radical ($^\bullet$O2$^-$) can also be produced by photochemistry in natural

surface waters and has the potential to oxidize Hg^0. $^{\cdot}O_2^{-}$ can both oxidize and reduce transition elements. It is considered to be a significant oxidant of Fe(II) (23). It thus appears that

- $^{\cdot}$OH and $^{\cdot}O_2^{-}$ could play a role in the oxidation of Hg^0, but it is not clear if these pathways are important in natural waters. In addition to these chemically driven reactions, biological processes involved in Hg^0 oxidation have received little attention.

We report here results of laboratory and field experiments designed to discern potential reaction mechanisms and to assess the depth to which Hg^0 oxidation occurs in natural water. Field experiments were conducted in the St. Lawrence River estuary, since our earlier work has already established that these brackish waters are sites of Hg^0 photooxidation (11). This estuary receives water from one of the world's largest drainage basins (1.3×10^6 km^2; 24), and knowledge of factors affecting fluxes of Hg at the interfaces of this large river is important in regional modeling of Hg (25, 26). First, we determined the wavelengths (visible, UV-A, or UV-B) responsible for Hg^0 oxidation in natural brackish waters by incubating samples from the St. Lawrence River under natural solar radiation and covering the incubation vessels with various sunlight filters. Second, we investigated the role of $^{\cdot}$OH and $^{\cdot}O_2^{-}$ in artificial and natural waters using specific radical scavengers. Last, we assessed the role of dissolved oxygen in Hg^0 oxidation and determined the importance of biologically driven oxidation of Hg^0 in natural waters.

TABLE 1. First-Order Rate of Hg^0 Oxidation Reported in the Literature for Natural Waters

location	k (h^{-1})	ref
Freshwaters		
Ranger Lake, ON	0.06	14
Florida Everglades, FL	0.1–0.6	15
Gouffre, Escoumin, and	0.2–0.3	11
St. Lawrence Rivers, PQ		
Freshwater pond, TN	0.2–0.3	13
Saline Waters		
Gulf of Mexico	0.1	10
St. Lawrence River Estuary, PQ	0.5–0.9	11
Gouffre River + Cl^{-} (0.5 M), PQ	0.7	11

Methods

Preparation of Solutions. Clean techniques were used during the experiments. The glassware was thoroughly cleaned by soaking in nitric (15% v/v; Baker instra-analyzed reagent, J.
T. Baker, Phillipsburg, NJ) and hydrochloric acids (2% v/v;
J. T. Baker) for approximately 24h. Gloves (hypoclean powder-free latex gloves, Safeskin, San Diego, CA) were worn at all times.

We spiked natural water samples and synthetic solutions with ca. nanomolar levels of Hg^0(aq) to observe Hg^0 photo-oxidation. Solutions of Hg^0(aq) were prepared by bubbling Milli-Q water with a N_2 gas flow containing Hg^0. Hg^0 was incorporated into the gas by letting it flow over a drop of liquid Hg (99.9999% Hg, reagent ACS, Aldrich, Milwaukee, WI) placed at the bottom of a U-shaped glass tube. The concentrations of Hg^0(aq) obtained by this method were 90 ± 40 n M. This solution was then used to spike the water sample with Hg^0(aq). Final Hg^0(aq) concentrations varied from 0.2 to 2.0 n M. The solution mixed in 1-L Teflon bottles was transferred in the incubation vessels. Note that natural Hg concentrations in the St. Lawrence River near Quebec City range from 0.5 to 12.9 pM for filtered Hg and from 0.2
to 1.5 pM for particulate Hg (24). DGM (dissolved gas mercury) concentrations range from 75 to 185 fM in the Upper St. Lawrence (26) and from <170 to 360 fM in the estuary (25).

Specific scavengers were used to determine the role of radicals in Hg^0 oxidation. Superoxide dismutase or SOD (4 n M; EC 1.15.1.1. from bovine erythrocytes, 5100 units (mg of protein)$^{-1}$, Sigma Chemical Co., St. Louis, MO) and methanol (0.01 M; environmental grade, Alfa Aesar, Ward Hill, MA) were used to scavenge $O_2^{\cdot-}$ (27) and $^{\cdot}$OH (28), respectively. We studied the effect of SOD and methanol in both natural waters and synthetic solutions. Synthetic

solutions were made with ultrapure water (>18 MΩcm^{-1}) buffered at p H 8 with a phosphate buffer (NaH$_2$PO$_4$ and Na$_2$HPO$_4$, both analytical reagents, BDH Inc., Toronto, Canada) cleaned by passing it through an ion-exchange resin column (Chelex-100 Na-form, type styrene lattice with iminodiacetic acid exchange groups; $75-150$ μm, Bio-Rad Laboratories). To these solutions we added 0.5 MKCl (reagent ACS, ACP, Montreal, Canada); 0.32 m M *p*-benzoquinone (Acros, New Jersey), which is known to produce semiquinone radicals upon irradiation (*29*); and Hg^0(aq). Semiquinones in the presence of Cl$^-$ are known to oxidize Hg ^{0}(*11*).

The role of dissolved oxygen in Hg ^{0} oxidation was assessed by comparing the Hg^0 oxidation rate in brackish waters spiked with Hg^0(aq) and incubated under a UV lam p to the Hg ^{0} oxidation rate obtained in low oxygen brackish water. Dissolved oxygen was removed by purging samples with ultra- high-purity argon, stripped of Hg ^{0} by passage over a gold filter. A bubbling control experiment was also done by purging brackish water with clean ambient air using a Tekran (model 1100) zero air generator to ensure that the bubbling itself did not affect the oxidation rate. Dissolved oxygen concentrations as measured at the end of the incubation experiments was 9 mg L^{-1} in the brackish water sample that was not bubbled, 0.9 mg L^{-1} in the argon-bubbled water sample, and 10 mg L^{-1} for the water sample bubbled with zero air.

Three tests were performed to determine if the observed photoinduced Hg ^{0} oxidation was due mostly to biotic or abiotic processes. First, we eliminated all living micro- organisms by adding chloroform (1:10 v/v; Honeywell Burdick & Jackson, Muskegon, MI) to natural water samples for 12 h. At the end of this period, chloroform formed a drop at the bottom of the solution that was removed from the water sample with a pipet. The remaining chloroform was degassed from the solution by purging it with cleaned ambient air for 2 h under a class 100, metal-free, laminar flow hood (Microzone Corp., Nepean, Canada, model V6-MW-99-C30). The calculated reaction rate obtained with the chloroform- treated water was com pared to the rate in a control experiment done with untreated natural water sampled at the same time and spiked with Hg ^{0} only. We further tested the importance of microorganisms by heat-sterilizing water samples for 3 h at 85 $\square$C or by filtering out microorganisms from natural water samples with an acid-cleaned cartridge with a porosity of 0.45 μm (Gelman Sciences, Ann Arbor, MI). Note that some oxygen may have been lost during sterilization by heating.

Sampling Site, Water Collection, and Ancillary Data Collection. Natural surface water was sampled before dawn (4:00 $-$ 4:30 a.m.) at Baie Saint-Paul in the estuary of the St. Lawrence River at high tides in order to sample salty water. Water samples were collected by filling 1-L FEP Teflon bottles (Nalgene, Rochester, NY) by hand at a depth of 0.5 m. On site, we measured p H (Hanna Instruments Inc., model HI9024 / HI9025, Woonsocket, RI) and dissolved oxygen (YSI Inc., model 50B, Yellow Springs, OH). The p H of the water samples was of 7.8 $\pm$ 0.1, and the dissolved oxygen con- centration varied little throughout the sampling time (9.4 $\pm$0.1 mg L^{-1}). Dissolved organic carbon was quantified with a Technicon auto-analyzer by persulfate-UV oxidation, followed by conductometric determination of the CO$_2$ released. Dissolved organic carbon concentrations varied from 4 to 6 mg of C L^{-1} with sampling time. Ca, K, and Na were measured by flame AAS (Varian SpectrAA-20), and Cl$^-$ and SO$_4^{2-}$ were measured by ion chromatography (Dionex AutoIon, system DX300) to confirm that salty water was sampled. Cl$^-$ concentrations ranged from 0.24 to 0.37 M, concentrations at which Hg ^{0} oxidation was observed in natural waters (*11*).

Incubation Setup. For all experiments, only freshwater collected on the day of the experiment was used. Therefore, each set of experiments was done with a different batch of bulk water, although every experiment within a given set was done with the same batch (for instance, Figures 1 and 2 correspond to two different sets of experiments). To conduct the polychromatic action spectra of Hg ^{0} oxidation, cutoff filters were wrapped over water samples contained in 80- mL quartz tubes placed in a water bath and incubated under the sun. Mylar filters were used to prevent UV-B irradiation, UV- Lee filters model 226 were used to prevent UV-B and UV-A irradiation, aluminum paper was used as a dark control, and no filter was used to allow the irradiation of UV and visible light. The incubation was done on the roof of the scientific com plex of INRS-ETE in Sainte-Foy, PQ, Canada (latitude, 46$\square$49$\square$N). The water bath was renewed continuously to maintain a constant water temperature of approximately 15 °C. The different light treatments were done on separate days during the first week of August 2000 under clear skies. Sunlight intensity was measured using a field spectroradiometer (Fieldspec VNIR, Analytical Spectral Devices, Boulder, CO).

The remaining incubation experiments were done in a constant temperature incubator at 17 $\square$C on a flat dark surface, 30 cm under a broadband UVB fluorescent bulb (FS20T12; 7 μE m^{-2} s^{-1}; maximal intensity centered at 312 n m) in transparent Teflon tubes (60 mL, Savillex Co., Minnetonka, MN) and in Teflon tubes wrapped in aluminum paper (dark treatment). Note that this lam p emits light over a broader range of wavelengths than UV-B (percent of total emission: PAR, 4%; UV-A, 32%; UV-B, 64%). UV-B intensities measured by ferrioxalate actinometry (*30*) varied slightly with tube position inside the incubator (5.62 $\pm$ 0.96 μE m^{-2} s^{-1}), corresponding to approximately 73% of midday UV-B intensity in July at our latitude (*11*).

Incubations under the sun or the UV-B lam p were done directly after the Hg ^{0}(aq) spikes. No headspace was present within the incubation vessels in order to prevent loss of Hg ^{0} by volatilization to the headspace. Hg ^{0} and total Hg concentrations were followed through time of incubation. Hg analyses were performed within minutes of the incubation period.
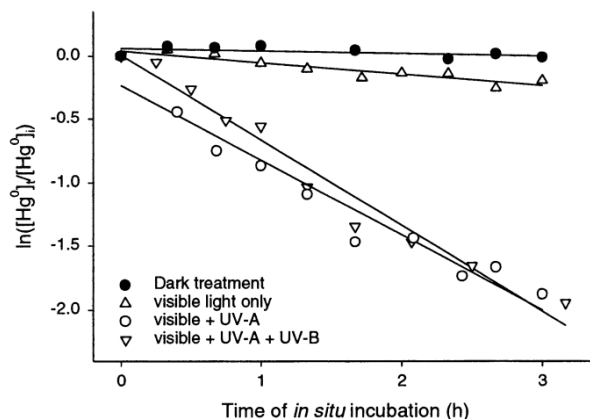
FIGURE 1. Polychromatic action spectra of Hg⁰ oxidation in natural brackish waters spiked with Hg⁰(aq) and incubated under the sun (latitude 46°49′ N) at 15 °C in unwrapped clear quartz reaction vessels (UV-A + UV-B + visible light treatment) or wrapped with sunlight cutoff filters such as Mylar (UV-A + visible light treatment) or UV-Lee filter model 226 (visible light only treatment). Dark treatments are reaction vessels wrapped in aluminum foil. Refer to Table 2 for corresponding Hg⁰ oxidation rates and UV-A, UV-B, and visible sunlight intensities.

Hg Analysis. Hg^0(aq) concentrations were analyzed by bubbling for 8 min a 60-mL solution in a glass bubbler using ultra-high-purity argon stripped of Hg^0 by passage over a gold filter, at a flow rate o f 1 L min $^{-1}$. The gas stream coming out of the bubbler was dried using a K_2CO_3 column (J. T. Baker). The Hg^0 transferred to the gas phase was collected on a gold wire trap (Brooks Rand Ltd, Seattle, WA). The trap was then placed in an argon gas stream, and the Hg was desorbed by pyrolysis at a flow rate of 60 mL min $^{-1}$ using a double gold amalgamation technique. The released Hg was quantified by gas-phase atomic fluorescence spectrometry (Tekran Hg analyzer, model 2500, Toronto, Canada). Total Hg concentrations were measured by reducing all of the Hg present in solution with $NaBH_4$ (0.5 mL of 1% $NaBH_4$ w/v + 0.5 mL of NaOH 4 M; both from J. T. Baker) prior to bubbling. The working detection limit of this method was calculated as 0.2 pM or three times the standard deviation of 10 blanks.

Calculation of Oxidation Rates. To identify at what wavelengths mercury oxidation was efficient, we carried out a series of photolysis reactions at different energy levels. In particular, we used visible (400 $< \lambda <$ 700 n m), UV-A (320 $< \lambda <$ 400 nm), and UV-B (280 $< \lambda <$ 320 nm) irradiation

$$Hg^0 + \frac{h\nu}{radical} \rightarrow products \tag{1}$$

We followed the concentration of Hg^0 as a function of time. Assuming the pseudo-first-order kinetic behavior of oxidation reactions, we can then simplify the rate equation to

$$\frac{-d[Hg^0]}{dt} = k_{ap}[Hg^0] \tag{2}$$

k_{ap} represents the apparent rate constant. In case of radical initiated oxidation of mercury $k_{ap} = k \times$[oxidant]. Integrated rate expression can be written as

$$\ln\left\{\frac{[Hg^0]_t}{[Hg^0]_i}\right\} = -k_{ap}t \tag{2}$$

where Hg^0 and Hg^0 represent initial concentration of mercury and concentration at time t, respectively. Hence, a plot of ln □ $[Hg]_t$/$[Hg]_i$ □ versus t should yield a negative slope with an absolute value equal to the apparent rate constant and a zero intercept.
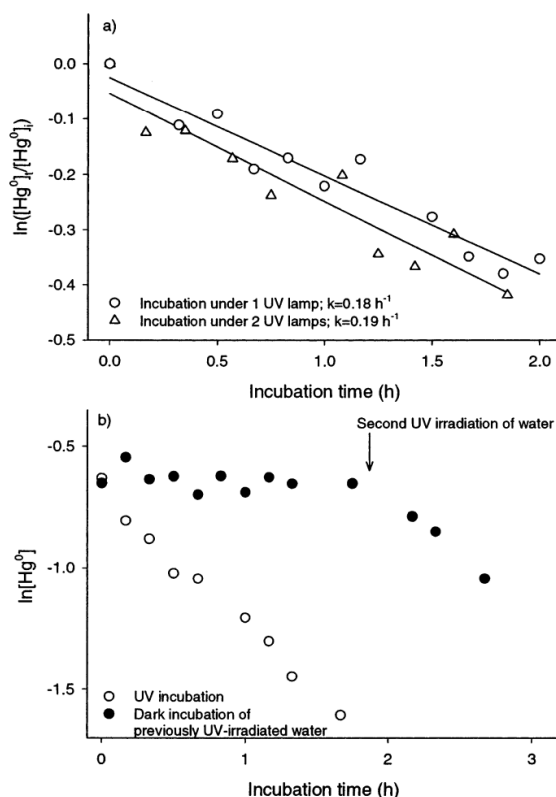
FIGURE 2. (a) Hg^0 photooxidation in natural brackish water spiked with $Hg^0(aq)$ and incubated under one UV-B lamp (circles) or two UV-B lamps (triangles). (b) "Direct" Hg^0 photooxidation in natural brackish water spiked with $Hg^0(aq)$ and incubated under a UV-B lamp (open circles), and "indirect" Hg^0 photooxidation where previously UV-irradiated brackish water was removed from the UV rays, spiked with $Hg^0(aq)$, and kept in the dark (closed circles) or incubated under the UV-B lamp again (after the arrow).

Statistical Analysis. Linear regressions were done to determine the reaction kinetics (*31*). Analyses of covariance were performed on the regressions of Hg ^{0} concentration versus incubation time of different treatments to test for homogeneity of slopes (*31*). The Bonferroni correction was used for pairwise com parisons (*31*). The null hypothesis was rejected when $p < 0.05$. All analyses were performed using SYSTAT version 10.01 software package for Windows (SPSS Inc., Chicago, IL).

TABLE 2. Hg^0 Oxidation Rates (Assuming a First-Order Kinetics) of Surface Brackish Water Spiked with $Hg^0(aq)$ and Incubated under the Sun in Uncovered Clear Quartz Reaction Vessels and in Reaction Vessels Wrapped with Various Sunlight Filters as Well as the Corresponding UV-B, UV-A, and Visible Light Intensities ($\mu E\ m^{-2}$)

	sunlight irradiance ($\mu E\ m^{-2}$)				
filter used	UV-B[a]	UV-A[b]	visible	k (h^{-1})	p^c
uncovered	0.049	1.42	18.6	0.67	<0.001
Mylar		1.10	15.9	0.59	<0.001
UV-Lee filter			10.7	0.09	<0.001
aluminum paper				0.02	0.14

[a] Data integrated between 290 and 320 nm obtained from Montreal's (Canada) Brewer spectroradiometer (station 319; latitude 45°47′ N).[b] Data integrated between 350 and 400 nm obtained from a field spectro-radiometer (Fieldspec VNIR, Analytical Spectral Devices, Boulder, CO). [c] The p values represent the results of regressions of Hg^0 concentration *versus* time of incubation.

Results and Discussion

Wavelengths Responsible for Hg^0 Oxidation. Hg^0 photo- oxidation is chiefly mediated by UV radiation in natural brackish waters (Figure 1; Table 2): "dark" oxidation was not found to be statistically significant, visible light induced a significant but slow photooxidation ($k = 0.09$ h^{-1}), while visible + UV-A and visible + UV-A + UV-B induced a rapid photooxidation ($k = 0.59$ and 0.67 h^{-1}, respectively). UV-B irradiation increased slightly but not statistically significantly the reaction rate of Hg^0 photooxidation from 0.59 to 0.67 h^{-1} (result of multiway analysis of the ANCOVA: $p = 0.12$; Table 2). We therefore estimate that UV-A irradiation is mostly responsible for Hg^0 oxidation in natural brackish waters from the St. Lawrence River spiked with Hg^0(aq) at ca. 0.5 nM and incubated under the sun at our latitude (46 □49 N). Note that we did not have a "UV-B only" treatment. Therefore it is possible that, in the absence of UV-A, UV-B radiation would have been effective in oxidizing Hg (see below the saturating effect of light intensity).

Effect of Light Intensity. In a previous study, we have already observed that Hg^0 is probably not the chromophore for its own photooxidation in synthetic solutions (ultrapure water, water + chloride, water + semiquinones) irradiated with environ mental levels of UV-B (*11*). Also, the data of Figure 1 show that UV-B irradiation did not yield significant oxidation of Hg^0, and thus the excitation of Hg^0 appears to be of minor importance under our experimental conditions. We observed further that doubling the intensity of the incident radiation had no effect on the rate of Hg^0 oxidation in natural water (Figure 2a). It thus appears that this oxidation is the result of a secondary photoreaction and that the formation of some excited intermediate may be limiting the reaction rate.

Study of Photoproduced Oxidants. We conducted parallel experiments where we monitored (i) "direct" Hg^0 photooxidation in natural estuary water spiked with Hg^0(aq) and incubated under a UV lam p, and (ii) "indirect" Hg^0 photo- oxidation in previously UV-irradiated (for 2 h) estuary water removed from the UV light, rapidly spiked with Hg^0(aq), and kept in the dark. In the first case, we observed a significant Hg^0 photooxidation ($k = 0.53$ h^{-1}, $p < 0.0001$; Figure 2b), but in the second case we observed no significant oxidation ($k = 0.03$ h^{-1}, $p = 0.31$; Figure 2b). In the latter case, when the water was UV-irradiated again, we observed Hg^0 photo- oxidation rates similar to the previously observed direct Hg^0 photooxidation ($k = 0.57$ h^{-1} vs $k = 0.53$ h^{-1}; see inset of Figure 2b). These results suggest that the intermediates responsible for Hg^0 oxidation are relatively short-lived (<5 min).

These new results are contrary to reports of subsequent dark oxidation after an initial sunlight incubation observed in the saline coastal waters of the Gulf of Mexico (*10*) and in freshwater (*13*, *15*). The observations made in saline coastal waters from the Gulf of Mexico could differ from ours since they were partly confounded by the important presence of particulate matter originating from the Mississippi River (*10*). However, those made in freshwater suggest that different and perhaps longer-lived Hg^0 oxidants were photoproduced in that study. Note also that past studies (*10*, *13*, *15)* were done at ambient DGM levels whereas this study was done using samples amended with Hg^0(aq). This Hg^0(aq) addition may have made it more difficult to see subtle changes in DGM levels during dark incubation.

O$_2^{\bullet-}$ (*32*) and $^\bullet$OH (*22*) are radicals believed to be photoproduced at rates sufficiently high to potentially affect chemical and biological processes in sunlit seawater. In natural brackish waters, the addition of methanol (a $^\bullet$OH scavenger; *28*) decreased by 25% the Hg^0 photooxidation rate ($k_{\text{control experiment}} = 0.43$ h^{-1} vs $k_{\text{methanol}} = 0.32$ h^{-1}; Figure 3a; a result of multi-way analysis of the ANCOVA: $p = 0.01$). Similar results were obtained with artificial saline water buffered at pH 8 containing semiquinones, where methanol slowed Hg photooxidation by 19% (Figure 3b). Note that $^\bullet$OH may have been formed in the system through secondary reactions following the initial scavenging of $^\bullet$OH by CH$_3$OH (e.g., ref *33*). However, since we added an excess of scavenger (0.01 M CH$_3$OH), we are confident that all $^\bullet$OH radicals were scavenged. This estimate of 25% reduction in the oxidation rate should still be viewed with caution since methanol can potentially also act as a scavenger for other reactive species beside $^\bullet$OH (such as Cl$^\bullet$ and HO$_2$). Previous studies have already concluded that methanol does not directly modify the oxidation state of Hg (*34*).

Superoxide dismutase (SOD), an enzyme that scavenges O$_2^{-\bullet}$ rapidly (*27*), did not influence the photooxidation rate in natural water ($k_{\text{control experiment}} = 0.43$ h^{-1} vs $k_{\text{SOD}} = 0.42$ h^{-1}; Figure 3a). In artificial saline water with semiquinones (Figure 3b), SOD slowed Hg^0 photooxidation by 18%, suggesting that O$_2^{\bullet-}$ may oxidize Hg^0 under some circumstances or that SOD interacted with semiquinones.

Overall, these results indicate that $^\bullet$OH likely plays a role in the oxidation of Hg^0 in natural surface waters while O$_2^{\bullet-}$ does not seem to be an important Hg^0 oxidant. Perhaps the increase in Hg^0 photooxidation rate observed when UV-B was added to visible and UV-A radiation (Table 2) could result from $^\bullet$OH formation, since Mopper and Zhou (*22*) showed that $^\bullet$OH is generated from UV-B irradiation of natural surface saline waters. $^\bullet$OH also fits our previous observations that Hg^0 oxidation is mediated by short-lived photoproduced oxidants since once produced in natural saline waters, it can be consumed within a few microseconds by reactants such as Br$^-$ (*35*). The hypothesis that $^\bullet$OH is partly responsible for the indirect photooxidation of Hg^0 fits well with our observations and deserves further study.

Effect of Dissolved Oxygen on Hg^0 Oxidation. Reducing the dissolved oxygen concentration from 9 to 0.9 mg L^{-1} in brackish water did not decrease the Hg^0 photooxidation rate (Figure 4). Therefore, dissolved oxygen is unlikely limiting Hg^0 photooxidation in natural brackish waters since the dissolved oxygen concentration in the well- mixed water column of this section of the St. Lawrence River is fairly constant and above 0.9 mg L^{-1} (9.4 ± 0.1 mg L^{-1}, $n = 10$). The limiting factors of Hg^0 photooxidation in the St. Lawrence River are more probably the penetration of UV-A within the water column (0.6 m; see below) and / or the presence of Hg^0 oxidants.
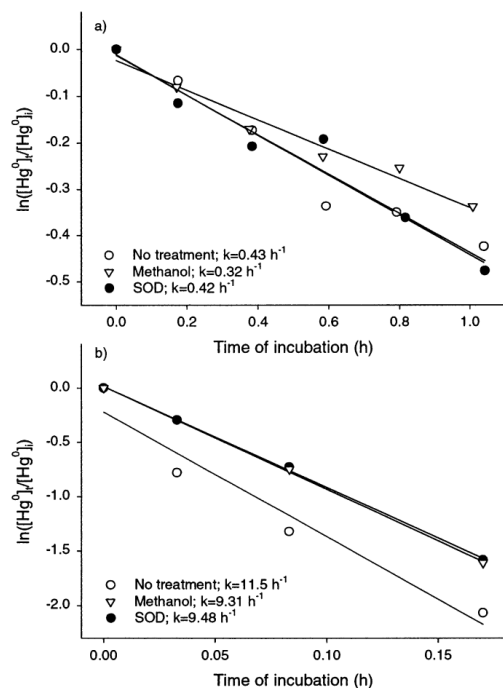
FIGURE 3. Effect of methanol (hydroxyl scavenger) and superoxide dismuthase (superoxide scavenger) on Hg^0 photooxidation rate in (a) surface brackish water spiked with Hg^0(aq) and incubated under a UV-B lamp and (b) artificial solutions of KCl (0.5 M), semiquinones, and Hg^0(aq) incubated under a UV-B lamp.
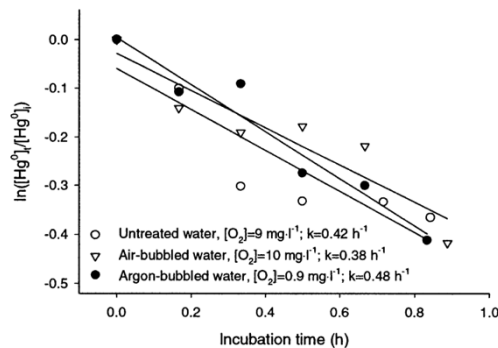

FIGURE 4. Effect of dissolved oxygen concentrations on Hg^0 photooxidation rate in surface brackish water spiked with Hg^0(aq) and incubated under a UV-B lamp.

Are Microorganisms Involved in Hg^0 Oxidation? To determine if microorganisms are somehow involved in the photoinduced oxidation of Hg^0, we studied the effect of chloroform, heat sterilization and water filtration (0.45 μm) on the reaction. We calculated similar reaction rates in untreated, chloroform-treated, and heat-sterilized natural water samples (Figure 5a,b). The elimination of living microorganisms by chloroform addition or heat-sterilization did not influence the reaction rate. Filtering out micro- organisms did not decrease the Hg^0 photooxidation rate but rather significantly increased it (Figure 5c). A decrease in Hg^0 photooxidation rates in the absence of living micro- organisms would have provided evidence of their role in the oxidation of Hg^0. We conclude that, on the time scale of these experiments (hours), microorganisms seem to have minimal involvement in the observed photoinduced Hg^0 oxidation in surface brackish waters of the St. Lawrence River.

The increased reaction rate of Hg^0 oxidation observed upon filtration (Figure 5c) has been observed in three different types of brackish waters over a 3-yr period (data not shown). Several hypotheses could explain these observations. For instance, particles present in the estuarine system could slow Hg^0 photooxidation by absorbing UV-A radiation (*36*). However, this hypothesis can be rejected since increasing light intensity did not result in an increase of Hg^0 photo-oxidation (Figure 2b). Alternatively, the opposite reaction (Hg(II) photoreduction) could be affected by filtration. We indeed observed lower Hg(II) photoreduction rates in filtered (0.45 μm) natural brackish waters spiked with Hg(II) (0.5 n M) as com pared to unfiltered waters (Figure 6). The increased net oxidation rates in filtered water could therefore be explained, at least in part, by a decrease in reduction rate. This Hg(II) photoreduction probably follows an abiotic heterogeneous process (involving nonliving particles). Al- though Hg(II) bioreduction in pristine waters has been reported before (*37−39*), it is unlikely to be significant in this case, since elimination of microorganisms by the addition of chloroform or by heat sterilization did not affect Hg^0 photooxidation or Hg(II) photoreduction rates. Other studies have also proposed that Hg(II) photoreduction in natural waters could involve heterogeneous processes (*16*, *40*).

Other explanations of increased Hg^0 photooxidation after filtration include differences in Hg^0 partitioning between filtered and unfiltered natural brackish water samples and differential scavenging of the photoproduced oxidants in the presence or absence of particles. Clearly, additional field and laboratory work will be necessary to establish the exact effect of particles on Hg(II) photoreduction.
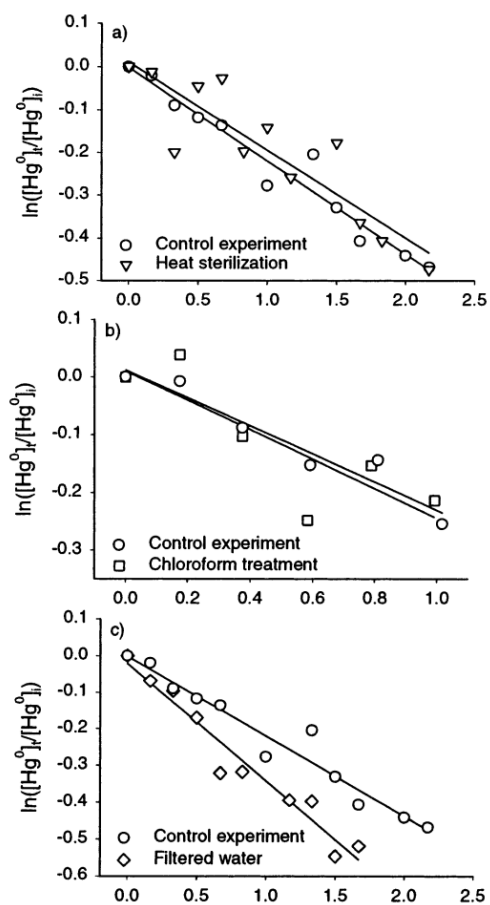
FIGURE 5. Effect of (a) chloroform, (b) heat sterilization, and (c) water filtration (0.45 μm) on Hg^0 photooxidation rate in surface brackish water spiked with Hg^0(aq) and incubated under a UV-B lamp.

Oxidation versus Volatilization. It was previously assumed that UV-B was needed to induce Hg^0 photooxidation (*11*), but our results indicate that UV-A induces Hg^0 photo- oxidation (Figure 1; Table 2). We must thus revise the previously calculated depth at which oxidation can occur (*11*) since UV-A can penetrate deeper than UV-B in the water column. As exemplified in the following calculation, it now appears that photooxidation should be relatively more important than volatilization in controlling Hg^0(aq) concentrations in surface waters.

We estimated the extinction coefficient (η) of UV-A for the St. Lawrence River to be 2.6 m^{-1} using the model equation of Scully and Lean (*41*) ($\eta_{UV-A} = 0.3$ [DOC (mg L^{-1})]$^{1.53}$) and the average DOC concentration measured in the St. Lawrence River (4.1 mg L^{-1}).

The calculated depth at which such a water column receives at least 1% of incident UV-A radiation is 1.8 m. We use the first-order rate constants from the polychromatic action spectrum (Figure 1), with the idea that they are applicable to the field at the depth of 1.8 m at noon in July. Considering a typical "piston velocity" of 1 cm h^{-1} (*42*) and a Hg^0(aq) concentration of 0.2 pM (the atmospheric concentration is negligible), we calculate a volatilization flux out of the water column of 7 pmol m^{-2} h^{-1} using the thin film model (fully described in ref *43*; see also ref *11*). By comparison, the loss of Hg^0 by photooxidation induced by UV-A (first-order $k = 0.6$ h^{-1}) would be ca. 300 pmol m^{-2} h^{-1} for a 1.8 m deep water column in seawater instead of the previously estimated 0.2 m (*11*). Therefore, in coastal waters such as those of the St. Lawrence River, photooxidation of Hg^0 is likely to be dominant during the summer days as compared to volatilization of Hg^0 from the water column, even in periods of high winds (when the piston velocity may increase up to 10 cm h^{-1}; *42*).

It is important to note that laboratory experiments in this study have been conducted under a UV lamp that primarily emitted UV-B radiation (62% UV-B, 32% UV-A), whereas we have shown that UV-A radiation was also important in Hg photooxidation. Future mechanistic studies on Hg photo- oxidation should therefore directly assess the role of UV-A radiation.
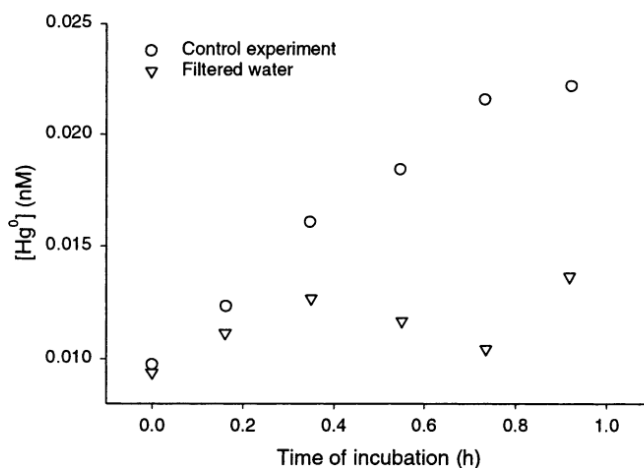
FIGURE 6. Effect of water filtration (0.45 μm) on photoinduced Hg(II) reduction in brackish waters spiked with Hg(II) (0.5 nM) and incubated under a UV-B lamp.

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