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# Photooxidation of Hg(0) in Artificial and Natural Waters

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The oxidation of volatile aqueous Hg(0) in aquatic systems may be important in reducing fluxes of Hg out of aquatic systems. Here we report the results of laboratory and field experiments designed to identify the parameters that control the photooxidation of Hg(0)(aq) and to assess the possible importance of this process in aquatic systems. The concentrations of elemental and total Hg were measured as a function of time in both artificial and natural waters irradiated with a UV-B lamp. No change in Hg speciation was observed in dark controls, while a significant decrease in Hg(0) was observed in UV-B irradiated artificial solutions containing both chloride ions and benzoquinone. Significant photooxidation rates were also measured in natural samples spiked with Hg(0)(aq); the photooxidation of Hg(0) then follows pseudo first-order kinetics ( $k = 0.6 \text{ h}^{-1}$ ). These results indicate that the previously observed Hg(II) photoreduction rates in natural waters could represent a net balance between Hg(II) photoreduction and Hg(0) photooxidation. As calculated from Hg(0) photooxidation rates, the dominant Hg(0) sink is likely to be photooxidation rather than volatilization from the water column during summer days.

## Introduction

Redox reactions of mercury are important in determining the fate of Hg in aquatic systems. The total mercury concentration in a water body is partly controlled by direct deposition from the atmosphere of the oxidized form, Hg(II), and by volatilization of the reduced form, Hg(0) (1). The loss of Hg from the water column is therefore enhanced by in situ Hg(II) reduction and decreased by Hg(0) oxidation.

While reduction, particularly photoreduction, of Hg(II) in aquatic systems has been fairly well studied (2–6), oxidation has been largely ignored because Hg(0) is typically considered to be unreactive. Nevertheless, recent laboratory experiments have demonstrated that, in oxygenated solutions containing sufficient chloride concentrations, liquid Hg(0) is effectively oxidized in the dark (7, 8). But it is not known if these results obtained with liquid drops of Hg(0) are relevant to natural waters containing low concentrations of dissolved Hg(0), Hg(0)(aq). Furthermore, the reaction mechanisms are unclear.

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In a field study in the coastal waters of the Gulf of Mexico, Amyot et al. (9) have observed that Hg(0)(aq) can undergo (dark) oxidation at a significant rate. In experiments with river water, these authors showed that the oxidation rate of Hg(0)(aq), like that of liquid Hg(0), is clearly enhanced in the presence of high  $\text{Cl}^-$  concentrations and also appears to depend on the presence of unidentified particles or colloids that can be removed by filtration. These experiments were partly confounded, however, by the loss of mercury from solution, either by volatilization of Hg(0) to the headspace of the container and/or adsorption of Hg(II) on the container walls.

In experiments designed to study the photoreduction of Hg(II) in field samples, it is common to observe a plateau in Hg(0) concentrations after 1–4 h (5, 6) and sometimes even a decrease in [Hg(0)(aq)] after the initial increase (9). Similar complex kinetics have previously been observed in the photoreduction of Fe(II) in natural waters and been shown to result from the accumulation of photoproducts (10). It thus seems possible that, in addition to dark oxidation, Hg(0) may be subject to photooxidation in natural waters.

Here we report the results of systematic laboratory and field experiments designed to determine the principal parameters that control the photooxidation of Hg(0)(aq) such as the concentrations of chloride and potential oxidants and to assess the possible importance of this process in aquatic systems.

## Experimental Section

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

To observe Hg(0) photooxidation in the laboratory, we prepared synthetic solutions with ultrapure water ( $> 18 \text{ M}\Omega \text{ cm}^{-1}$ ) buffered at pH 8 with a phosphate buffer ( $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , 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  $\mu\text{m}$ , BioRad Laboratories). The solutions were spiked with Hg(0)(aq).

Solutions of Hg(0)(aq) were prepared by bubbling Milli-Q water with a  $\text{N}_2$  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  $90 \pm 40 \text{ nM}$ . This solution was then used to spike the water sample with Hg(0)(aq). Final Hg concentrations varied from 0.2 to 2.0 nM.

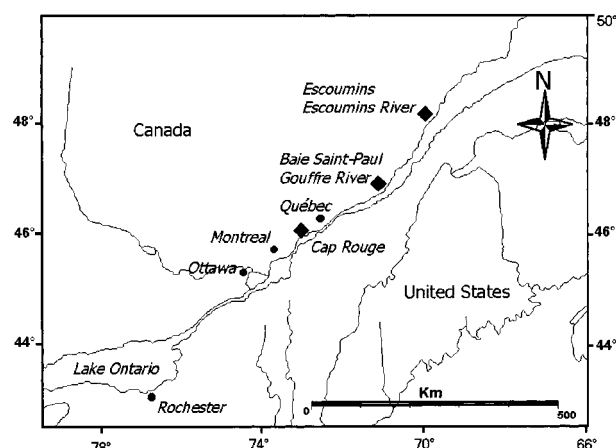
To test the importance of the concentrations of chloride and semiquinones on Hg(0) oxidation, we conducted experiments in the presence and absence of 0.5 M KCl (reagent ACS, ACP, Montreal, Canada) and 0, 0.16, and 0.32 mM *p*-benzoquinone (Acros, NJ).

**Sampling Sites, Water Collection, and Ancillary Data Collection.** Three sampling sites along the St. Lawrence River were chosen for their different salinity (Table 1; Figure 1). The lowest salinity site was located at the marina of Cap Rouge at the end of a dock; a higher salinity site was situated at Baie Saint-Paul, and the highest salinity site was in Baie des Escoumins. At these last two sites, water samples were collected from shore. Gouffre River, a tributary of Baie Saint-

**TABLE 1. First-Order Rate of Hg(0) Photooxidation (and Pertinent Cl<sup>-</sup> and Dissolved Organic Carbon (DOC) Concentrations) Measured in Irradiated Surface Samples of the St. Lawrence River and Tributaries Spiked with Various Concentrations of Hg(0)(aq)**

date (dd/mm/yy)	location	[Hg(0)] <sup>a</sup> (nM)	k <sup>b</sup> (h <sup>-1</sup> )	[Cl <sup>-</sup> ] (M) (n = 2)	[DOC] (mg C L <sup>-1</sup> ) (n = 2)
Freshwater					
01/09/99	Cap Rouge	0.73	0.23	4.8–5.3 × 10 <sup>-4</sup>	4.0–4.3
08/08/99	Escoumins River	0.80	0.26	5.1–5.2 × 10 <sup>-4</sup>	3.5
22/07/99	Gouffre River	0.85	0.26	4.7–5.0 × 10 <sup>-4</sup>	4.0–3.8
		x̄ ± s.d. 0.25 ± 0.02			
Saline Water					
26/07/99	Baie Saint-Paul	0.74	0.64	0.23–0.24	3.4–4.3
10/08/99		0.30	0.72	0.25–0.26	5.9–3.7
10/08/99		1.30	0.86	0.25–0.26	5.9–3.7
10/08/99		2.00	0.73	0.25–0.26	5.9–3.7
17/08/99		0.77	0.54	0.18	4.2–4.9
25/08/99		1.00	0.69	0.26	3.5–3.8
01/08/99	Baie Escoumins	0.63	0.58	0.34–0.37	4.0–3.7
		x̄ ± s.d. 0.67 ± 0.10			
Freshwater + KCl (0.5 M)					
22/07/99	Gouffre River	0.75	0.56	0.5	4.0–3.8

<sup>a</sup> The Hg(0) concentrations represent the initial Hg(0) spike to the water sample. <sup>b</sup> The initial rate was calculated using data obtained during the first hour of the experiments.



**FIGURE 1. Sampling sites along the St. Lawrence River.**

Paul, and Escoumins River, a tributary of Baie des Escoumins, were also sampled from shore.

Water samples were collected by filling 1 L FEP Teflon bottles (Nalgene, Rochester, NY) by hand at a depth of 0.5 m. Water samples were taken at high tides (to sample salty water) and before sunrise (to prevent the formation of organic radicals that could influence Hg(0) photooxidation before the start of the experiments). pH (Hanna Instrument Inc. model HI9024/HI9025, Woonsocket, USA) and dissolved oxygen (YSI Inc. model 50B, Yellow Springs, USA) were sampled on site. The pH ( $7.8 \pm 0.1$  in Baie Saint-Paul,  $8.26 \pm 0.01$  in Cap Rouge,  $7.94$  in Baie des Escoumins, and  $7.0 \pm 0.1$  in both tributaries) and dissolved oxygen concentrations ( $9.4 \pm 0.1$  mg L<sup>-1</sup> throughout sampling sites and dates) were measured on site. Dissolved organic carbon was measured by filtering water on site (filter porosity of  $0.45 \mu\text{m}$ , Acrodisc; Gelman Sciences, Ann Arbor, MI) and quantifying the total carbon content with a Technicon Auto-Analyzer by persulfate-UV oxidation, followed by conductometric determination of the CO<sub>2</sub> released. Ca, K, and Na were measured by Flame AAS (Varian SpectraAA-20), and Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> by ion chromatography (Dionex AutoIon, system DX300).

**Incubation Experiments.** Unspiked natural water samples were incubated in 1 L Teflon bottles under a UV-B lamp for 3 h (see below). In the course of the incubation, an aliquot was taken every 30 min, and Hg(0) and total Hg concentra-

tions were measured. In subsequent experiments the (photo)-oxidation of Hg(0) was followed in natural water samples spiked with nanomolar levels of Hg(0)(aq). The solution, premixed in 1 L Teflon bottles, was transferred to unwrapped and foil-wrapped 64 mL Teflon tubes that were incubated flat on a dark sheet at 30 cm from the UV-B lamp for 3 h and analyzed every 15 min.

**UV-B Incubation Setup.** Both artificial saline solution and natural water samples were incubated immediately after the Hg(0)(aq) spike at 17 °C on a flat dark surface at 30 cm from a UV-B neon lamp (FS20T12-UV-B medical lamp, USA) in transparent Teflon tubes (60 mL, Saville Co., Minnetonka, USA) and in Teflon tubes wrapped in aluminum foil (dark treatment). No headspace was present within the incubation tubes to prevent loss of Hg(0) by volatilization to the headspace. Hg(0) and total Hg concentrations were followed throughout the time of incubation. Hg analysis was performed within minutes of the end of the incubation period.

**Analysis of Hg.** Hg(0)(aq) concentrations were analyzed by bubbling for 8 min a 60 mL solution in a glass bubbler using ultrahigh-purity nitrogen stripped of Hg(0) by passage over a gold filter, at a flow rate of 1 L min<sup>-1</sup>. The gas stream coming out of the bubbler was dried using a K<sub>2</sub>CO<sub>3</sub> column (J. T. Baker, Phillipsburg, USA). 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<sup>-1</sup> using the double gold amalgamation technique (1). 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<sub>4</sub> (0.5 mL of 1% NaBH<sub>4</sub> w/v + 0.5 mL of 4 M NaOH; both from J. T. Baker, Phillipsburg, USA) prior to bubbling.

For analysis of Hg(0)(aq) in unspiked water samples, 500 mL of sample was purged in a Teflon bubbler for 15 min with ultrahigh-purity nitrogen stripped of Hg(0) by passage over a gold filter, at a flow rate of 1 L min<sup>-1</sup>. Volatile mercury compounds were trapped on a gold wire trap (Brooks Rand Ltd, Seattle, WA), desorbed by pyrolysis at a flow rate of 60 mL min<sup>-1</sup>, and quantified by gas-phase atomic fluorescence spectrometry (single amalgamation technique; see refs 1, 5, and 6). The gold trap was air-dried for 3 min before it was desorbed to prevent humidity from reaching the Hg analyzer.

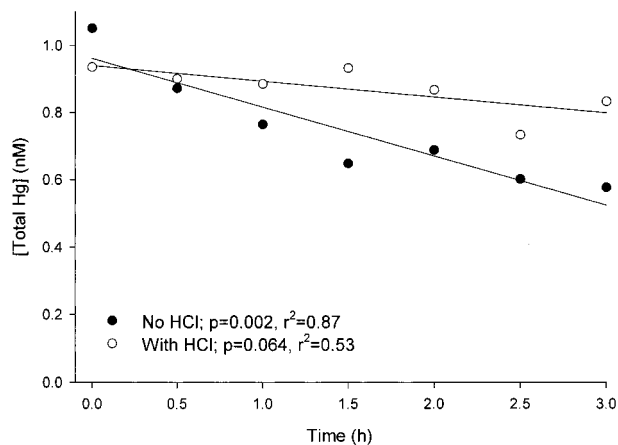
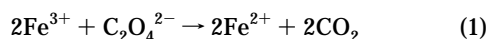


FIGURE 2. Total Hg concentrations in surface saline waters from Baie Saint-Paul vs time of incubation under a UV-B lamp in clear Teflon tubes. Closed circles: no acid added. Open circles: HCl (0.8 M) was added 1 h before analysis.

**Elimination of Artifacts.** In some incubation experiments with natural water samples, we observed a decrease in total Hg concentrations with time (Figure 2). This decrease could result either from adsorption of Hg(II) on the walls of the Teflon tube after Hg(0) oxidation or from Hg(0) volatilization through the walls of the tube. When 0.8 M HCl was added 1 h before analysis, almost all the initial Hg concentration was recovered, showing that the bulk of the apparent decrease with time resulted not from volatilization of Hg(0) but rather from adsorption of Hg(II) (Figure 2). Furthermore, Hg(0) levels did not decrease in dark experiments with synthetic water (see Figure 3e). Also, the evolution of Hg(0) concentration in dark experiments conducted with filtered (0.45  $\mu$ m) and unfiltered natural water was similar, indicating that Hg(0) does not adsorb onto particles (data not shown). We thus considered the decrease in Hg(0) concentration to represent Hg(0) oxidation in our experiments.

**Actinometry.** The light intensity through the Teflon tubes and the Teflon bottles used for incubation was calculated by the method of Hatchard et al. (11) modified by Murov and Dekker (12). This technique uses the photoreduction of ferric iron by potassium ferrioxalate



where the ferrous ion is determined via spectrophotometric determination of its phenanthroline complex at 510 nm. As seen in Table 2, the lamp used in our incubator gives out limited amounts of PAR and UV-A compared to the noon sun. The total intensity measured by actinometry in the Teflon bottles (1 L) at 30 cm is close to the total intensity recorded by the spectroradiometer (FieldSpec Pro, Analytical Spectral Devices, Inc., USA) at 30 cm of the incubation lamp while the total intensity measured by actinometry in the Teflon tubes (64 mL) is half the intensity of the incubation lamp. UV-B intensity measured at 30 cm under the incubation lamp with the spectroradiometer is less than half the UV-B intensity emitted by a noon July sun at latitude 46°48'N (Table 2). UV-B intensities measured by actinometry inside the Teflon bottles (1 L) and tubes (64 mL) were, respectively, approximately 30% and 20% of the UV-B intensity emitted by a noon July sun (Table 2).

## Results

**Hg(0) Photooxidation in Artificial Solutions.** No significant oxidation of Hg(0) was observed in buffered solutions of Hg(0)(aq) irradiated with UV-B radiation in either the absence (Figure 3a) or the presence of chloride (0.5 M; Figure 3b).

Addition of *p*-benzoquinone (32 nM), which is known to produce semiquinone radicals upon irradiation (13), had no effect in the absence of chloride (Figure 3c). When both chloride and benzoquinone were present, however, Hg(0)(aq) was rapidly (on the order of minutes) and completely oxidized in the light (Figure 3d). No oxidation was observed in the dark control (Figure 3e).

At the nanomolar mercury concentrations utilized in these experiments, the dimeric Hg(I) species,  $\text{Hg}_2^{2+}$ , can become an important part of the dissolved mercury pool and contribute to the oxidation of Hg(0), either as a final product or as an intermediate in the oxidation reaction. We thus repeated the experiment with an approximately 20 times lower Hg(0)(aq) concentration (130 pM) so that the formation of  $\text{Hg}_2^{2+}$  should be negligible (14). The results were virtually identical to those obtained at high concentrations (Figure 3f).

In natural waters, it is expected that reactive radical species such as semiquinones are produced as a result of redox reactions of humic substances, particularly as a result of UV irradiation. We thus performed a Hg(0) photooxidation experiment similar to that of Figure 3d but in which the benzoquinone was replaced by 15.4 nM of Aldrich fulvic acid. Surprisingly, we observed little oxidation of Hg(0) in this experiment (Figure 3g). This apparently constant Hg(0) concentration could be the result of a simultaneous oxidation of Hg(0) and increased reduction of Hg(II) by fulvic acid as compared to benzoquinone.

**Hg(0) Photooxidation in Natural Waters.** During the first 1.5 h of irradiation with a UV-B lamp, unspiked natural samples of Baie Saint-Paul water showed an increase in Hg(0) concentration (Figure 4). Such Hg(II) photoreduction to Hg(0) has been previously observed in several experiments (1, 5, 9). This increase in Hg(0) was followed by a subsequent decrease which could be indicative of Hg(0) photooxidation.

To observe oxidation of Hg(0) without the influence of Hg(II) reduction, we spiked natural water samples with Hg(0)(aq) to increase its concentration to the nanomolar range. With the addition of Hg(0)(aq) we observed photooxidation of Hg(0) in surface water samples at all the sampling sites. The rate of oxidation of Hg(0) in water from Baie Saint-Paul kept in the dark is significant, but about 10 times slower than that kept in the light ( $k = 0.06 \text{ h}^{-1}$  vs  $k = 0.58 \text{ h}^{-1}$ ), assuming first-order kinetics (Figure 5a).

The linearity of the logarithmic plot in Figure 5a implies that Hg(0) photooxidation probably follows pseudo first-order kinetics (when chloride concentration and UV radiation are kept constant). We verified that this is the case by performing the same experiment with different initial concentrations of Hg(0)(aq) (Figure 5b). All the logarithmically transformed data indeed follow approximately the same straight line. Further, the coefficient of variation of reaction rates were smallest when first-order rather than zero- or second-order kinetics were assumed (10% as compared to 66% and 92%, respectively).

To establish that the chloride concentration plays a critical role in the photooxidation of Hg(0)(aq) in field samples, as it does in laboratory samples, we examined the photooxidation of Hg(0)(aq) in spiked samples of Gouffre River water, with and without addition of 0.5 M KCl (Figure 6). The results show a doubling in the rate of Hg(0)(aq) photooxidation resulting from the chloride addition, although the photooxidation rate of the sample without added chloride is already quite high ( $k = 0.26 \text{ h}^{-1}$ ).

A tabulation of the photooxidation data from all our field experiments (Table 1) shows a clear difference between the rate constants measured in freshwater samples (0.23–0.26  $\text{h}^{-1}$ ) and those in marine samples (0.54–0.87  $\text{h}^{-1}$ ). Nonetheless, the range in photooxidation rate constants of the marine samples is relatively large.

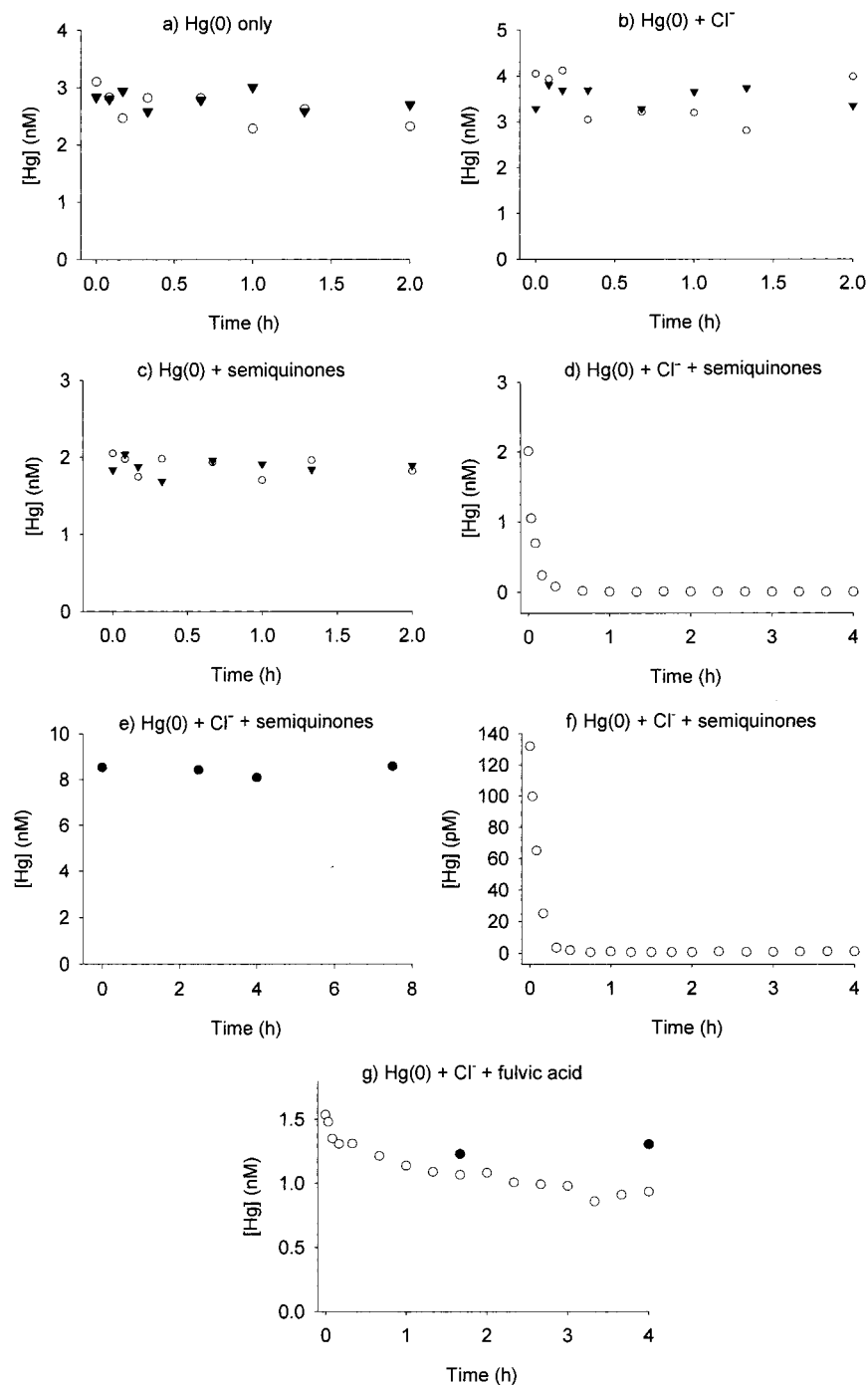


FIGURE 3. Oxidation of Hg(0) in artificial solutions of (a) Hg(0)(aq) only, (b) Hg(0)(aq) and chloride ions (0.5 M), (c) Hg(0)(aq) and semiquinones, (d) Hg(0)(aq), chloride ions, and semiquinones, (e) Hg(0)(aq), chloride ions (0.5 M), and semiquinones (dark controls), (f) lower concentrations of Hg(0)(aq) chloride ions (0.5 M) and semiquinones, and (g) Hg(0)(aq) chloride ions (0.5 M) and fulvic acid. All solutions were buffered at pH 8 with a clean phosphate buffer. The open symbols represent water samples irradiated with a UV-B lamp, and closed circles represent Hg(0) concentrations in dark experiments. Circles and triangles represent Hg(0) and total Hg concentrations, respectively.

## Discussion

We observed remarkably rapid oxidation of dissolved elemental mercury, Hg(0)(aq), both in the laboratory and in field samples upon irradiation under appropriate conditions. This observation should lead us to reevaluate the results of Hg(II) photoreduction experiments in which Hg(0) reoxidation has usually been assumed to be negligible (2–6). The steady state of Hg(0)(aq) concentration typically observed in freshwater samples after a few hours of incubation could possibly represent in part a balance of Hg(II) photoreduction and Hg(0) photooxidation. In seawater samples, Hg(0)(aq)

concentrations often decrease after 1–4 h of irradiation (e.g., Figure 4). We hypothesize that this may result from the accumulation of photoproducts (see below).

Our laboratory experiments demonstrate that oxidation of Hg(0)(aq) requires the simultaneous presence of chloride, of a photoreactive compound (benzoquinone), and of light. There is thus little doubt that this oxidation is the result of an indirect photochemical process, in which an electron acceptor produced by the chromophore is somehow able to promote effective oxidation of Hg(0)(aq) in the presence of chloride. In our model laboratory system, we know that



TABLE 2. PAR, UV-A, and UV-B Measurements Taken under the Noon Sun in July at Latitude 46°48'N and the UV-B Lamp (FS20T12 UV-B) Used in the Incubator<sup>a</sup>

	PAR ( $\mu\text{E m}^{-2} \text{s}^{-1}$ )	UV-A ( $\mu\text{E m}^{-2} \text{s}^{-1}$ )	UV-B ( $\mu\text{E m}^{-2} \text{s}^{-1}$ )	total ( $\mu\text{E m}^{-2} \text{s}^{-1}$ )
sun	1014	134	5.5	1154
UV-B lamp	5.41	5.42	2.32	13.2
Teflon bottles (1 L)	4.25	4.26	1.82	10.37
Teflon tubes (64 mL)	2.75	2.76	1.18	6.71

<sup>a</sup> Measurements in the incubator were recorded at 30 cm from the UV-B lamp with a spectroradiometer (FieldSpec Pro) and with an actinometer in two different Teflon containers irradiated with the UV-B lamp.

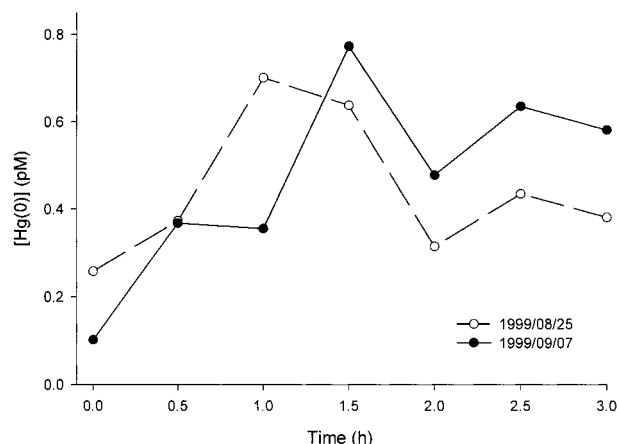


FIGURE 4. Evolution of Hg(0) concentrations in unspiked surface saline water from Baie Saint-Paul during two incubation experiments under a UV-B lamp.

semiquinone radicals are produced from benzoquinone in the light. But the standard potentials of semiquinones, 0.70 V vs NHE at pH = 7 (calculated from Rich & Bendall (15)), is not high enough to oxidize Hg(0)(aq) to the very unstable Hg<sup>+</sup> in water, since the redox potential of the Hg(I)/Hg(0) couple is ca. 1.3 V vs NHE at pH = 7 (calculated from Cartledge (16)). We thus hypothesize that the role of the chloride ion may be to stabilize Hg<sup>+</sup> in solution and decrease the Hg(I)/Hg(0) potential by several hundred millivolts to allow the transfer of an electron to the semiquinone. Oxidation of the hypothesized Hg(I)-Cl<sup>-</sup> complex by oxygen might then be rapid. Detailed laboratory experiments will be necessary to test this hypothetical mechanism of indirect photooxidation of Hg(0)(aq). Further studies would also be needed to test if this mechanism is the important one in the observed Hg(0) photooxidation in natural waters.

In the experiments done with natural waters, it is notable that, unlike what is observed in the laboratory, a significant rate of Hg(0)(aq) photooxidation is observed even in the absence of added chloride. If our hypothesis concerning the role of chloride as a complexing ligand for Hg<sup>+</sup> is correct, then either enough chloride is present in the freshwater samples, or some other inorganic or organic ligand is an effective complexing agent for Hg(I). Another explanation is that different mechanisms occur in natural and artificial water. At a concentration of chloride ions of ca. 0.5 mM, we know that Hg(II) is complexed by chloride ions principally in the form of HgCl<sub>2</sub> (17). The similarity of the rates observed in the various freshwater samples (Table 1), when only the irradiation rate was maintained constant, implies that neither the concentration of chromophore (to yield the reactive

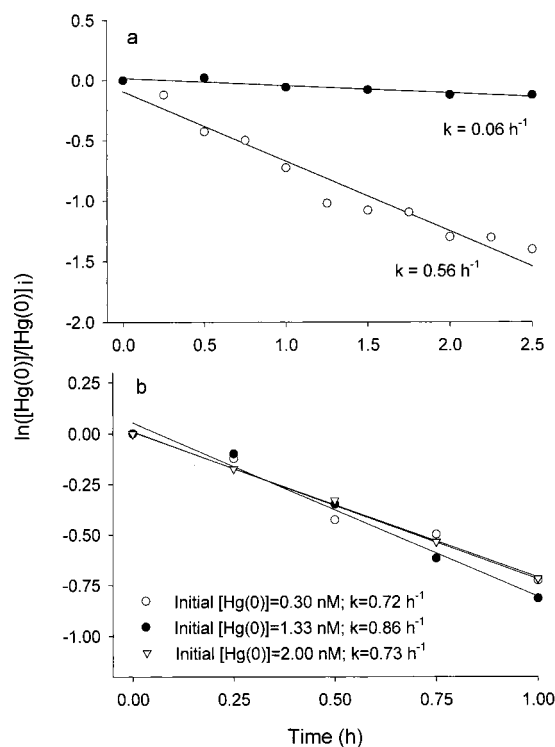


FIGURE 5. Kinetics of the oxidation of Hg(0) in saline surface waters of Baie Saint-Paul spiked with Hg(0)(aq): (a) Hg(0) photooxidation (open circles, initial [Hg(0)] = 0.33 nM) and dark oxidation (closed circles, initial [Hg(0)] = 0.21 nM); (b) Hg(0) photooxidation rates in samples of varying initial Hg(0)(aq) spike assuming a first-order kinetics. The Hg(0) photooxidation rates were obtained from irradiation of water samples to a UV-B lamp.

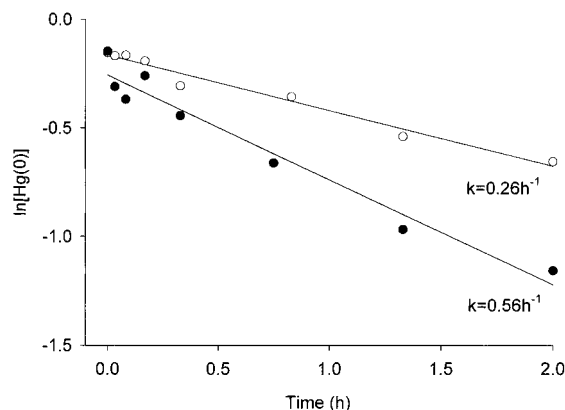


FIGURE 6. Reaction rates in surface freshwater from Cap Rouge spiked with Hg(0)(aq) with and without KCl (0.5 M).

oxidant) nor that of the hypothesized Hg(I) ligand were limiting.

UV-B radiation in the incubated Teflon tubes represented approximately 20% of the net solar radiation at the surface of the water column at midday in July at latitude 46°48'N (Table 2). We estimated the extinction coefficient ( $\eta$ ) of UV-B for the St. Lawrence River to be 5.73 m<sup>-1</sup> using the model equation of Scully and Lean (18) ( $\eta \text{ UV-B} = 0.415 \times [\text{DOC (mg L}^{-1})]^{1.86}$ ) and the average DOC concentration measured in the St. Lawrence (4.1 mg L<sup>-1</sup>; Table 1). The calculated depth at which such a water column receives at least 20% of incident UV-B radiation is 0.3 m. In the following, we use the first-order rate constants we measured in bottles, with the idea that they are applicable to the field at the depth of 0.3 m at noon in July.

Our field data are few and preliminary, but, with all the appropriate caveats, they can serve to provide a first evaluation of the possible importance of  $\text{Hg(0)(aq)}$  photooxidation in the cycling of Hg in surface waters. The relative importance of photooxidation and volatilization processes in controlling  $\text{Hg(0)(aq)}$  concentrations in surface waters can be assessed by comparing their rates. Considering, for example, a typical "piston velocity" of  $1 \text{ m d}^{-1}$  and a  $\text{Hg(0)(aq)}$  concentration of  $0.2 \text{ pM}$  (the atmospheric concentration is negligible), we calculate a volatilization flux out of the water column of  $7 \text{ pmol m}^{-2} \text{ d}^{-1}$ . By comparison, the loss of  $\text{Hg(0)}$  by photooxidation (first-order  $k = 0.25 \text{ h}^{-1}$  for freshwater and  $0.67 \text{ h}^{-1}$  for seawater) would be ca.  $15 \text{ nmol m}^{-2} \text{ d}^{-1}$  for a  $0.3 \text{ m}$  deep water column in freshwater and about  $40 \text{ nmol m}^{-2} \text{ d}^{-1}$  in seawater. Therefore, even in shallow waters such as those of the St. Lawrence River, photooxidation of  $\text{Hg(0)}$  is likely to be dominant during the summer days as compared to the volatilization of  $\text{Hg(0)}$  from the water column, except in periods of high winds (when the piston velocity may increase up to  $10 \text{ m d}^{-1}$ ).

The other major process determining the ambient concentration of  $\text{Hg(0)(aq)}$  in natural waters is the (photo)-reduction of  $\text{Hg(II)}$  to form  $\text{Hg(0)}$ . Amyot et al. (1) observed an initial first-order rate constant for  $\text{Hg(II)}$  photoreduction in the freshwater section of the St. Lawrence River to be between  $1$  and  $2 \text{ h}^{-1}$ . The reaction rates of Amyot et al. (1) were obtained by irradiating the water samples spiked with  $\text{Hg(II)}$  with 10 times the UV-B intensity as compared to our experimental method. Once normalized for the photon flux, we find that the light induced redox processes,  $\text{Hg(II)}$  reduction and  $\text{Hg(0)}$  oxidation, could occur at roughly similar rates in natural waters provided that the reaction rates observed in water samples incubated under a UV-B lamp would be equivalent to those incubated under the sunlight. Action spectra of  $\text{Hg(II)}$  (photo)reduction and  $\text{Hg(0)}$  (photo)oxidation would be needed to confirm this hypothesis.

Additional field and laboratory work will be necessary to establish the mechanisms and rates of photoredox reactions of mercury in surface waters. Nonetheless, it is now clear that the photooxidation of  $\text{Hg(0)}$  should be taken in account, both in calculating mercury budgets in aquatic systems and in sampling protocols which must consider the highly dynamic nature of the  $\text{Hg(0)(aq)}$  pool and the diel variations in sunlight.

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