Dark Oxidation of Dissolved and Liquid Elemental Mercury in Aquatic Environments

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Elemental mercury (Hg^0) can be found in liquid or dissolved forms in aquatic systems. Whereas dissolved Hg^0 is measured in virtually all aquatic systems, liquid Hg^0 droplets are mainly observed at poorly lit sediment/water interfaces of ecosystems with local point sources such as hydrothermal vents, gold extraction sites, and near industrial facilities. Here, we report that, in the dark, liquid and dissolved forms of Hg behave differently with respect to their oxidation. Liquid Hg^0 is rapidly oxidized in oxygenated solution in the presence of chloride. Liquid Hg^0 oxidation rates are positively correlated with chloride concentrations and droplet surface area. When liquid Hg is removed from solution, the oxidation stops even though the solution is still saturated with dissolved Hg^0. Liquid Hg^0 droplets in oxygenated marine or brackish environments should be oxidized and release Hg^{2+} to solution. In freshwaters or anoxic seawater, liquid Hg will dissolve releasing Hg_{aq}^0 which, itself, will slowly oxidize.

Introduction

Elemental mercury, Hg^0, can be found in liquid or dissolved forms in aquatic ecosystems. Dissolved Hg^0 is ubiquitous and usually shows higher concentrations near the surface, as a result of photoreduction of Hg(II) (*1*). Liquid Hg^0 is rarely observed in uncontaminated fresh or marine waters but may be present near local point sources. Typical examples include the release of liquid Hg in rivers and estuaries by gold mining activities (*2*). Offshore submarine hydrothermal vents have also been identified as significant sources of liquid Hg to the seafloor (*3*). In contrast to dissolved Hg^0, elemental Hg droplets are only found in sediments and at sediment/water interfaces. These environments are typically poorly lit and unlikely to be affected by photochemical processes.

Elemental Hg is the main volatile form of Hg in natural waters (*4*−*6*). The formation of volatile dissolved mercury favors the removal of Hg from lakes and ocean through gas evasion. On a local scale, this may be significant in the regulation of Hg accumulation in aquatic wildlife by de creasing the Hg burden in the water column at a given site and by limiting the amount of Hg available for methylation and bioaccumulation. On a global scale, Hg^0 evasion from the ocean surface constitutes a significant part of the global Hg cycle, accounting for about 40% of the current total flux of Hg to the atmosphere (*7*). It is therefore important to understand the processes leading to the formation of dissolved Hg^0 and to its oxidation.

While Hg(II) reduction in the aquatic environment has been relatively well studied (*8*−*13*), there is limited information on Hg^0 oxidation. Some field studies have suggested that dark oxidation of dissolved Hg^0 occurs in lakes (*14*) and coastal waters (*11*). Lalonde et al. (*15*−*16*) have shown that this oxidation is greatly enhanced by solar radiation, particularly UVB radiation, and by chloride. 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. Laboratory experiments have also shown that drops of liquid Hg^0 are oxidized when placed in water in the presence of chloride or thiol compounds and oxygen (*17*−*21*), whereas only limited oxidation occurs in the absence of chloride. However, these laboratory studies did not distinguish between oxidation at the surface of the liquid Hg^0 and of the dissolved Hg^0 at equilibrium with the liquid. To understand the potential fate of liquid Hg^0 in the environment, we need to quantify its rates of surface oxidation and dissolution and compare them to the rate of oxidation of dissolved Hg^0

The main objective of this study is to assess the differences in the oxidation of liquid and dissolved Hg^0 in aquatic environments. Since liquid droplets are mainly found in poorly lit environments (i.e., sediments and sediment/water interfaces), our focus here is on Hg oxidation in the dark. The specific goals are (a) to determine if oxidation of liquid Hg^0 occurs under the same conditions of salinity and oxygenation as oxidation of dissolved Hg^0 and (b) to compare the rates of oxidation and dissolution of liquid Hg^0 with the rate of oxidation of dissolved Hg^0.

Experimental Section

Experiments with Dissolved Hg^0. Solutions of dissolved Hg^0 were prepared by bubbling N_2 or O_2 containing Hg^0 vapor through Milli-Q water (Millipore). The gas was initially enriched with Hg^0 vapor by letting it flow over a drop of liquid Hg (ACS reagent grade, Aldrich, Milwaukee, WI) placed at the bottom of a U-shaped glass tube. The drop was prevented from moving downstream by a glass frit. The concentrations of dissolved mercury obtained by this method were in the 20−100 nM range. This solution was then diluted 1:10 in Milli-Q water to yield a final concentration in the 2−10 nM range. This range of concentrations is higher than what is usually observed in aquatic environments. However, this range is appropriate when considering dissolved Hg^0 levels likely to be observed in water overlying Hg droplets at sediment/water interfaces. All experiments were conducted in a reaction vessel containing 100 mL of solution.

Concentrations of dissolved Hg^0 and of total Hg (Hg_T) were followed over time (ranging from 2 to 6 h) in the diluted solution, under different concentrations of oxygen (hypoxic and saturated conditions), chloride (0, 5, and 500 μM), and hydrogen ions (at pH 5 and 7).

Dissolved Hg^0 analysis was performed by transferring 0.1 mL from the solution to a bubbler containing 300 mL of purged water and by bubbling for 12 min using a flow of purified Argon. The Hg^0 transferred to the gas phase was then collected on a gold wire trap (Brooks Rand, WA). Three gold traps were used for collection during this study. Their collection efficiency was routinely monitored and exceeded 90%. The collection traps were then placed in ultrahigh purity argon gas stream and the Hg was released by heating and recaptured by a second gold wire trap (double gold amalgamation technique). This second trap was heated and the released Hg was measured by an atomic fluorescence detector (Tekran Hg analyzer, model 2500, Canada). Calibrations were made using liquid standards or by injecting known amounts of gaseous

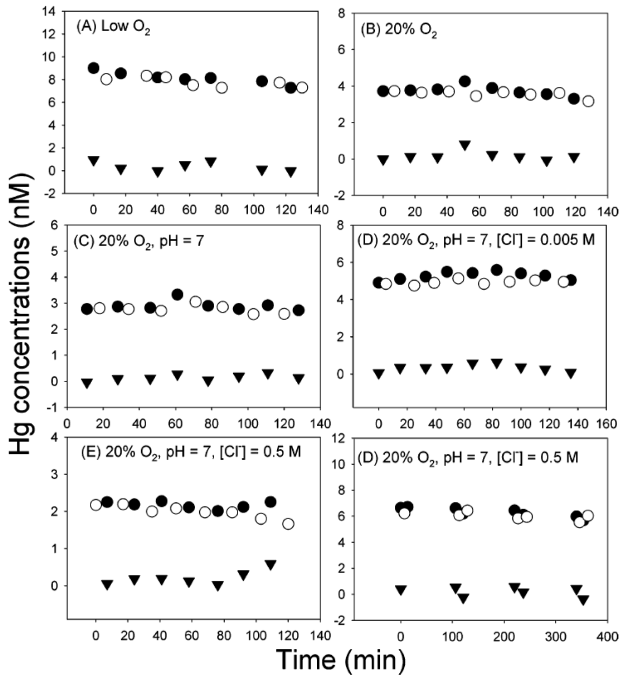

FIGURE 1. Time series of Hg^0 (open circles), Hg_T (closed squares), and Hg(I+II) (closed triangles) concentrations in Milli-Q water, at different concentrations of chloride and oxygen. 20% O_2 indicates that the samples are in equilibrium with air and dissolved oxygen is near saturation in solution. Hg(I+II) concentrations were calculated by the difference between Hg_T and Hg^0.

Hg^0 in the analytical line. Both methods yielded similar calibration curves. The detection limit of this method (calculated as 3 times the standard deviation of 10 low-level samples) was 0.06 nM.

For Hg_T, the pH of the sample was increased by addition of 1 mL NaOH (4 M). All the Hg was then immediately converted to Hg^0 using $NaBH_4$ (1 mL of 1% $NaBH_4$ w/v) as a reducing agent (*22*). The sample was then bubbled and Hg was measured as dissolved Hg^0. All glassware was thoroughly cleaned in acid and gloves were worn at all times. The detection limit of this method (calculated as 3 times the standard deviation of 10 low-level samples) was 0.04 nM.

Experiments with Liquid Hg^0. A drop of Hg^0 (Fisher; 0.1 mL) was placed in a 100-mL solution of Milli-Q water buffered at different pHs. Concentrations of dissolved Hg^0 and Hg_T were followed over time at different dissolved oxygen (0.70 and 8.85 mg L^{-1}) and chloride concentrations in solution (0, 5, 50, and 500 μM). We also investigated the effect of the size of the mercury droplet (0.011, 0.024, and 0.100 mL) on Hg oxidation over time, at constant chloride and oxygen levels. The effect of removing the Hg droplet after a 1-h exposure to a salted buffered and oxygenated solution was also studied. At these nanomolar concentrations of Hg^0, newly formed Hg(II) can potentially disproportionate into Hg^{2+}, since the disproportionation constant is about 5.2 nM at 25°C (*23*). We thus consider that the difference between the concentrations of total and elemental Hg corresponds to the sum of [Hg(I)] and [Hg(II)], referred below as Hg(I+II).

Results and Discussion

The oxidation of dissolved Hg^0 in the presence and absence of oxygen and chloride and at different pHs was followed over time (Figure 1). Dissolved Hg^0 was not rapidly oxidized by O_2 and chloride. These results contrast with those of Magalhães and Tubino (*18*) and Yamamoto (*20*) which showed an oxidation of droplets of liquid Hg^0 under similar conditions. They do agree with results obtained by Lalonde et al. (*15*, *16*), in which brackish waters kept in the dark did not show a significant loss of dissolved Hg^0 over time. It is therefore likely that liquid Hg^0 is more readily oxidized in the dark than dissolved Hg^0.

We observed indeed a rapid oxidation of liquid Hg^0 in the presence of chloride (Figure 2). After addition of KCl, Hg(II) levels increased at a rate of 13.5 nM min^{-1} ($r = 0.99$; $p < 0.001$; $n = 5$). The drop of Hg was then removed and oxidation of Hg^0 stopped immediately, even though approximately 200 nM of dissolved Hg^0 was still in solution. The chloride dependency of liquid Hg oxidation was further evidenced by changes in Hg oxidation rates when we varied the concentration of sodium chloride over 3 orders of magnitude (Figure 3A), in a solution equilibrated with ambient air and containing a 0.1-mL droplet of Hg^0. At the lowest $[Cl^-]$ (5 mM), the rate of Hg(II) production was similar to the one observed in the absence of chloride (Figure 3B). At higher $[Cl^-]$ (50–500 mM), the rate of oxidation was chloride-dependent.

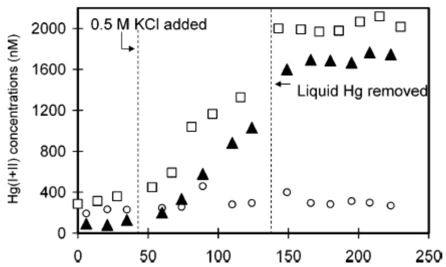

FIGURE 2. Time series of Hg^0 (open circles), Hg_T (open squares), and Hg(I+II) (closed triangles) concentrations in Milli-Q water equilibrated with ambient air, buffered at pH 7, in the presence of a Hg drop of 0.1 mL. Hg(I+II) concentrations were calculated by the difference between Hg_T and Hg^0. After 45 min, 0.5 M KCl was added and after 140 min, the Hg drop was removed. Hg(I+II) concentrations were calculated by the difference between Hg_T and Hg^0.

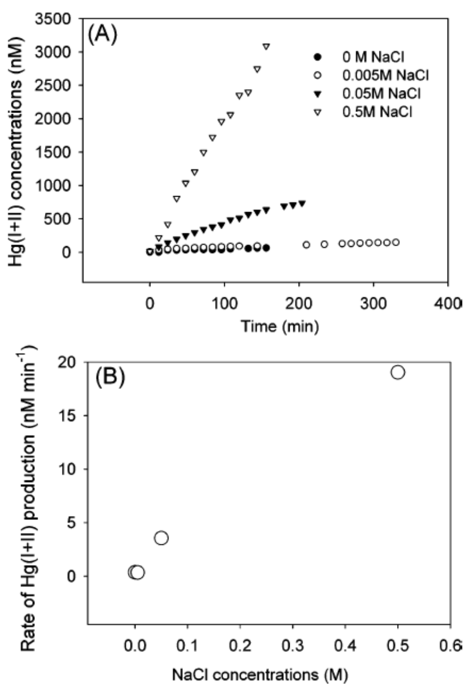

FIGURE 3. (A) Time series of Hg(I+II) formation in the presence of a 0.1-mL Hg^0 droplet, as a function of different levels of NaCl (0, 0.005, 0.05, 0.5 M) in a 100-mL aqueous solution equilibrated with ambient air. (B) Relationships between rates of Hg(I+II) production and different levels of NaCl. Hg(I+II) concentrations were calculated by the difference between Hg_T and Hg^0.

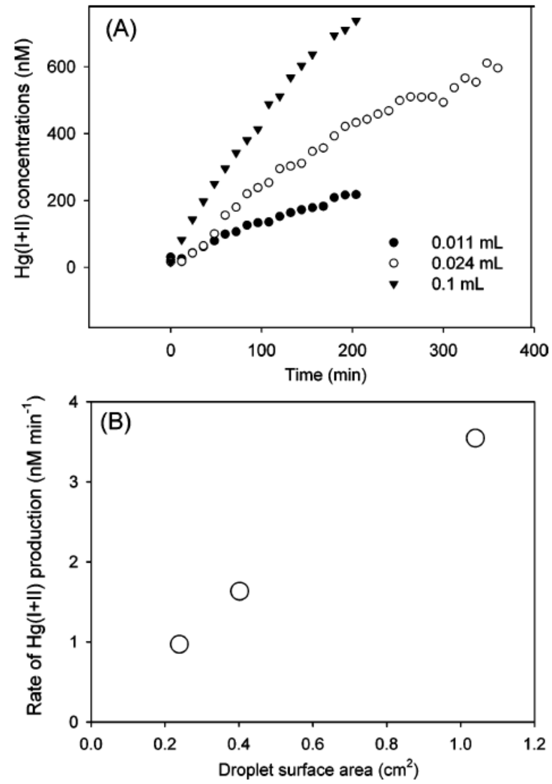

FIGURE 4. (A) Time series of Hg(I+II) formation, as a function of different droplet size (0.011, 0.024, 0.1 mL) in a 100-mL aqueous solution containing 0.05 M NaCl, equilibrated with ambient air. (B) Relationships between rates of Hg(I+II) production and different droplet surface areas. Hg(I+II) concentrations were calculated by the difference between Hg_T and Hg^0.

Since the approximate average concentration of chloride in natural freshwaters is around 8.3 mg L^{-1} (0.2 mM; *24*), liquid Hg^0 oxidation should be slow in freshwaters. In brackish or marine water, however, this oxidation may be relatively rapid.

Since the oxidation of Hg^0 ceased upon removal of the liquid droplet, it appears that the interface Hg^0 liquid/solution plays a critical role in the process. We thus examined the effect of changing the surface area of the droplet by varying its volume over an order of magnitude (0.01, 0.02, and 0.1 mL; Figure 4A), in a 100-mL solution equilibrated with ambient air and containing 0.05 M NaCl. Hg oxidation was faster in the presence of the larger drop but did not increase by an order of magnitude. As expected, the production of Hg(II) was proportional to the droplet surface area calculated by assuming that the droplet is roughly spherical (Figure 4B).

We tested the effect of oxygen concentration on the dark oxidation of liquid Hg^0 at an intermediate chloride concentration (0.05 M). At low oxygen levels (8.0% saturation), Hg oxidation was much slower than at high oxygen levels (99.5% saturation), with the initial oxidation rate roughly proportional to the concentration of O_2 (Figure 5A). These results are consistent with those reported by others (*18–19*). The higher oxidation rate observed at the higher O_2 concentration was matched by a markedly lower rate of dissolution of Hg^0 (Figure 5B). Because this effect was observed at the onset of the experiment, it probably reflects a competition for reactive mercury atoms between the two surface processes rather than a modification of the surface by oxidation as may be seen over longer time periods (see below). Both the rate of dissolution and the rate of oxidation of liquid Hg^0 slow with time (Figure 5). In dissolution, this is simply a reflection of the fact that equilibrium with the solution (ca. 200nM Hg_{aq}^0) is being approached. However, the decreasing rate of oxidation with time must reflect a decrease in the intrinsic rate of reaction at the surface. We hypothesize that oxidation products are being formed at the surface of the droplet, hampering further oxidation of Hg^0 over time.

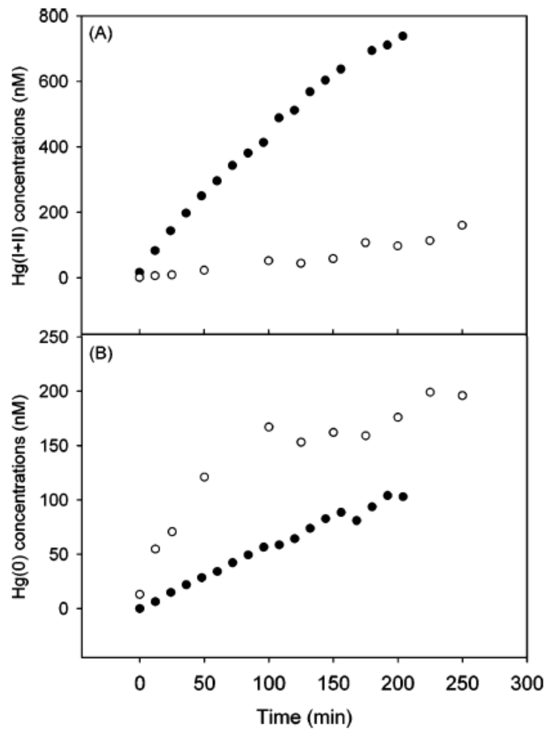

FIGURE 5. Time series of (A) Hg(I+II) concentrations and (B) Hg(0) concentrations at high (99.5% saturation) and low (8.0% saturation) oxygen levels, in the presence of a 0.1-mL Hg^0 droplet, in a 100-mL solution containing 0.05 M NaCl. Hg(I+II) concentrations were calculated by the difference between Hg_T and Hg^0.

To compare the rate of oxidation of liquid Hg^0 with that of Hg^0 in solution, we need to normalize it to the number of atoms of Hg^0 at the surface of the droplet. A simple calculation shows that this number is about $3(MN/m)^{2/3}$, where M is the mass of the droplet, m the atomic mass of Hg, and N Avogadro's number. The net result is that the concentration of surface atoms on a mercury droplet of 0.1 mL (1.36 g) in a 100-mL beaker must be approximately 10 nM. Thus, in an air-equilibrated solution at a concentration of chloride near that of seawater (0.5 M; see Figure 3), the surface of the droplet is oxidized with an approximate first- order rate constant of 2 min^{-1}, 2–3 orders of magnitude faster than Hg^0 in solution, even in the presence of solar radiation (k ranging between 0.002 and 0.015 min^{-1}; *16*). The same calculation for the rate of dissolution of liquid Hg^0 shows that the first-order rate constant (normalized to the concentration of surface atoms) is about 0.3 min^{-1}, ap- proximately the same as the rate of oxidation in 0.05 M NaCl (air-equilibrated). The total Hg^0 concentration contributed by a 0.1-mL droplet in a 100-mL beaker is 68 mM, and the half-life of such a droplet is 30 years if it is subjected only to dissolution (and if the initial dissolution rate we observed is maintained by efficient diffusion/advection of the dissolved Hg^0 that is produced). Oxidation in oxygenated seawater would reduce this half-life to about 5 years, if the initial rate of oxidation were maintained, (presumably by sufficient agitation of the droplet to avoid "pacification" of the surface).

Liquid Hg droplets are currently found (i) near sites of gold and mercury extraction, (ii) near some hydrothermal vents, and (iii) near industrial point sources. Our results indicate that drops of Hg^0 should be oxidized and release Hg^{2+} to solution if they are present in brackish or marine oxygenated waters, such as the estuaries of rivers where gold extraction is conducted. Mercury drops present in low salinity or anoxic waters, including hydrothermal vents, should gradually dissolve, releasing Hg^0 to solution. From previous experiments, we determined that dissolved Hg^0 can be oxidized in the dark in the presence of oxygen, chloride, and a suitable surface. In coastal systems, first-order oxidation rate constants reached values around 0.1 h^{-1} (*11*). Further research is needed to understand the role of adsorption at natural interfaces in such oxidation and to compare the resulting oxidation rates with those observed for liquid mercury.

Acknowledgments

This research was supported by grants from U.S. EPA to F.M.M.M. and from NSERC and the Collaborative Mercury Research Network to M.A. We thank Dominic Bélanger for his analytical contribution.

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