

Diel variations in photoinduced oxidation of Hg^0 in freshwater

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Abstract

Experiments have been conducted to determine diel variations in photoinduced Hg^0 oxidation in lake water under natural $\text{Hg}^0_{(\text{aq})}$ concentrations. Pseudo-first-order rates of photooxidation (k') were calculated for water freshly collected in a Canadian Shield lake, Lake Croche (45°56'N, 74°00'W), at different periods of the day and subsequently incubated in the dark. Hg^0 oxidation rates ranged from 0.02 to 0.07 h^{-1} , increasing from sunrise to noon and then decreasing throughout the remainder of the day. These changes paralleled those in sunlight intensity integrated over 1 h preceding water collection, and suggested that the water freshly collected in daylight was rich in photochemically produced Hg^0 oxidants. It was also estimated that under intense solar radiation, even if oxidation rates reached a peak, reduction of $\text{Hg}(\text{II})$ was the prevalent redox process. Inversely, Hg^0 oxidation overcame DGM production during the night or at periods of weaker light intensity. Overall, these findings explain the decreases in the DGM pool generally observed overnight. They also support previous reports that, during summer days, volatilization of Hg^0 from water represents an important step in the Hg cycle in freshwater systems.

1. Introduction

The cycling of Hg between its reduced and oxidized forms in natural waters plays an important role in its fate in the environment. Reduction of $\text{Hg}(\text{II})$ to dissolved gaseous mercury (DGM), mostly as volatile Hg^0 , has been identified as an important mechanism of loss of Hg to the atmosphere (Mason and Fitzgerald, 1993; Rolfs and Fitzgerald, 2001). Oxidation of Hg^0 , in contrast, may increase the pool of $\text{Hg}(\text{II})$ in an aquatic system, ultimately affecting Hg accumulation by the aquatic biota.

In aquatic systems, solar radiation in the UV and visible ranges influences the production of DGM (Amyot et al., 1994; Amyot et al., 1997a; Costa and Liss, 1999). As a consequence, DGM concentrations tend to follow a diel pattern, being the highest around noon and the lowest during the night. Dissolved organic carbon (DOC) and ferric iron are thought to be as mediators in the $\text{Hg}(\text{II})$ photoreduction (Matthiessen, 1996; Lindberg et al., 2000; Zhang and Lindberg, 2001). The biotic production of DGM has also been observed (Mason et al., 1995; Lanzillotta et al., 2004). Laboratory and field experiments have shown that Hg^0 photooxidation is stimulated in the simultaneous presence of chloride and semiquinones (Lalonde et al., 2001). This finding explains higher photooxidation rates observed in seawater and estuaries relatively to freshwaters (Amyot et al., 1997b; Lalonde et al., 2004). In freshwater, oxidation in the dark has been observed (Amyot et al., 1997a; Zhang and Lindberg, 2001), but diel trends and mechanisms involved in the oxidation processes have been less extensively studied. The aim of this study is to investigate diel variations in the rates of sunlight-induced Hg^0 oxidation in lake water under natural DGM concentrations. Considering that reduction and oxidation of Hg can be both photochemically driven, this work also contributes to a better understanding of the balance between both processes in natural waters.

2. Methods

The experiments were conducted in Lake Croche, a small (5.31 km^2) slightly colored ($\text{DOC} = 3.5 \text{ mg l}^{-1}$) oligotrophic lake located at the Laurentian Biological Station of the University of Montreal on the Canadian Shield (45°56' N, 74°00' W).

Subsurface water samples were taken in a 6-m deep portion of the lake during summer 2003. Samples were collected by hand, using quartz bottles (ø 8 cm - 40 cm). No headspace was present within the incubation bottles to avoid loss of Hg^0 by volatilization to the headspace. Clean procedures were adopted during sample collection and analysis: powder-free latex gloves were worn at all times; the glassware was soaked in 20% HNO_3 and rinsed three times with Milli-Q water, and the sampling bottles were rinsed three times with lake water prior to use.

To assess dark oxidation, samples were collected on July 22 around 23:00 in order to avoid the presence of photoreactive radicals during the experiment. DGM was then measured at 30-min intervals during 4 h.

To observe diel variations in sunlight-induced Hg^0 oxidation, samples were collected on July 23 at different times of the day: 6:30, 9:30, 12:30, 15:30, 18:30 and 21:30. For each period, samples were

kept in the dark, in a cooler, for up to 5 h. Samples in duplicate or triplicate were then analyzed for DGM at 30-min or 1-h intervals from time 0 to time 5 h. Loss of DOC fluorescence in lake water was used as a proxy for the photoreactants production. DOC fluorescence was measured at 1-h intervals at 355 nm excitation and 455 nm emission wavelengths. A 0.05 M H₂SO₄ solution was used as a blank. Values were calibrated against the fluorescence of quinine sulfate using standard solutions, with one quinine sulfate unit (QSU) = 1 ppb quinine sulfate in 0.05 M H₂SO₄.

To compare the rates of Hg(II) reduction and Hg⁰ oxidation, water was sampled on July 25 at 6:20, 9:20, 12:50, 16:00 and 19:00. At each period, 15 samples were collected. Three samples were immediately analyzed for DGM, while three others were kept in a cooler for 2 h as controls for dark oxidation or reduction. The remaining nine samples were submerged in an 8-cm deep water bath and exposed to full surface solar radiation spectrum to induce the production of photoreductants and photooxidants. The water bath temperature was kept constant through water replacement. After 1 h, three samples were analyzed for DGM, three others were placed in the dark, in a cooler, and three samples were kept under natural sunlight for another hour. DGM concentrations were measured at the end of the incubation period, and variations in DGM concentrations were calculated for the dark and light treatments at different periods of the day.

In all experiments DGM analyses were performed within minutes of the end of the incubation period. Approximately 500 ml of water was slowly decanted into 1-l glass bubblers and purged for 15 min with Hg-free air with a Tekran 1100 zero air generator. The volatile Hg compounds were trapped on a gold-coated sand column. The trap was dried for 3 min in an argon air stream and Hg was subsequently desorbed by pyrolysis at a flow rate of 60 ml min⁻¹, using the double amalgamation technique. Hg was quantified by gas-phase atomic fluorescence spectrometry with Tekran Hg analyzer model 2500. In this study, simultaneous analyses of replicates were possible due to the use of two analytical lines, each one consisting of two bubblers coupled to one Hg-free air generator and one Hg detector. Quality control was achieved through the intercalibration of the two lines, as well as by processing 3 or 4 system blank checks before the beginning of the analysis. For the intercalibration, water from Lake Croche was collected ~4 h after sunset in order to minimize the influence of photoreductants or photooxidants. Samples (*n* = 30) were taken using either quartz or Teflon bottles, stored in a cooler, and DGM was immediately measured simultaneously in the two analytical lines. Results from this intercalibration exercise indicated a good correspondence between the two lines: $91.6 \pm 6.3 \text{ pg l}^{-1}$ and $88.9 \pm 4.8 \text{ pg l}^{-1}$.

Solar radiation in the visible range (400–700 nm) was measured during the incubations with a Li-Cor photometer. Light measurements in the UVB range were obtained from the weather station of the Laurentian Biological Station of the University of Montreal.

3. Results and discussions

3.1.1. Hg⁰ photoinduced oxidation rates

DGM concentrations in freshly-collected surface water sampled at different periods of the day and immediately placed in the dark tended to decrease over time (Fig. 1). The observed decreases in DGM concentration were primarily attributed to oxidation of Hg⁰, and followed pseudo-first-order kinetics, as described by Eq. (1), rather than zero- or second-order kinetics:

$$\ln \left\{ \frac{[\text{Hg}^0]_t}{[\text{Hg}^0]_0} \right\} = -k't \quad (1)$$

where [Hg⁰]_{*t*} and [Hg⁰]₀ represent DGM concentrations at time *t* and at the beginning of the incubations, respectively. *k'* is the apparent rate of oxidation of Hg⁰ and corresponds, in absolute value, to the slope of the regression of ln{[Hg⁰]_{*t*}/[Hg⁰]₀} versus *t*. Clearly, assumption of linear behavior cannot completely describe the observation, particularly in light of scattered data. However, this approximation seems to be valid in explaining the pattern observed during incubation experiments. We speculate that the scatter in the data can result from:

(a) a gradual loss of photolytically-initiated oxidants and/or (b) the presence of different types of Hg⁰ oxidants. Following light exposure, photooxidants would prevail over dark oxidants, increasing

the oxidation rates of Hg^0 . With the gradual degradation of photoinduced oxidants, only slower dark oxidation reaction could proceed.

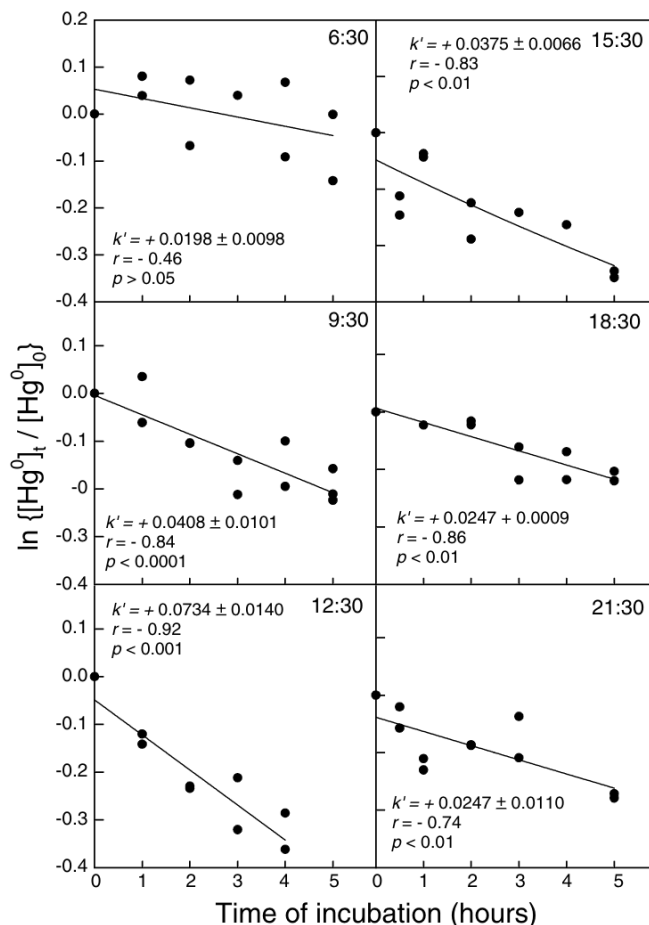


Fig. 1. Hg^0 photooxidation in subsurface water samples from Lake Croche collected at 6:30, 9:30, 12:30, 15:30, 18:30 and 21:30 on July 23, 2003, and incubated in the dark.

We attempted more complex kinetic expressions to more appropriately describe the observed data than with simple pseudo-first-order kinetics (e.g. consecutive reactions, intermediates via equilibria, multiple equilibria; see Steinfeld et al., 1998). However, none could more adequately describe our observations. Hence, we continued employing Eq.(1). Note that using more complex kinetic expressions than a simple pseudo-first-order equation (1) will not necessarily yield to more information for further interpreting our field data. Since the detailed chemical reactions are not known (e.g., intermediates, consecutive reactions, parallel reactions; see Steinfeld et al., 1998), various approximations will lead to an overall apparent exponential expression that can equally be described by Eq.(1).

The oxidation rates of Hg^0 varied from $\sim 0.02 \text{ h}^{-1}$ to 0.07 h^{-1} (Fig. 1) and were significantly different from 0 ($p < 0.05$), except for k' estimated for samples collected at the beginning of the day (at 6:30). This range is around one-order of magnitude lower than oxidation rates observed in saline waters or in natural water exposed to UVB lamps and spiked either with $\text{Hg}^0_{(\text{aq})}$ or KCl (k' between 0.2 and 0.9 h^{-1} ; Lalonde et al., 2001) or than the rate observed in a pond water spiked with Fe(III) ($k' = 0.2 \text{ h}^{-1}$; Zhang and Lindberg, 2001). Note however that the present study was conducted using freshwater containing natural DGM concentrations (between 59 and 79 pg l^{-1}) and exposed to sunlight; it constitutes thus a clear evidence of the occurrence of Hg^0 oxidation in freshwater systems under natural

conditions.

The oxidation rates of Hg^0 in surface water of Lake Croche varied over the course of the day and followed a sinusoidal pattern (Fig. 2): k' values increased from sunrise to noon and decreased afterward. Therefore, oxidation rates of Hg^0 can be separated into three groups. The first one corresponds to samples collected at 12:30, under more intense solar radiation, with the highest k' value (0.073 h^{-1}). The second group consists of samples collected in the middle of morning (at 9:30) or of afternoon (at 15:30), with intermediate values of k' (0.041 and 0.038 h^{-1} , respectively). The third group includes samples collected at dawn, at dusk or in the evening, exhibiting the slowest rates of oxidation ($k' 0.020$ – 0.025 h^{-1}). In fact, these slower rates were similar to rates observed under dark oxidation ($k' = 0.024$, Fig. 3). Overall, these results suggest that oxidation of Hg^0 is stimulated by solar radiation. Indeed, a cross correlation analysis indicated a high correlation between k' and the photosynthetically active radiation (PAR, $\lambda = 400$ – 700 nm) or UVB radiation at time lags of 15–75 min (r between 0.90 and 0.95). These findings are consistent with those of Zhang and Lindberg (2001), who observed a faster decrease

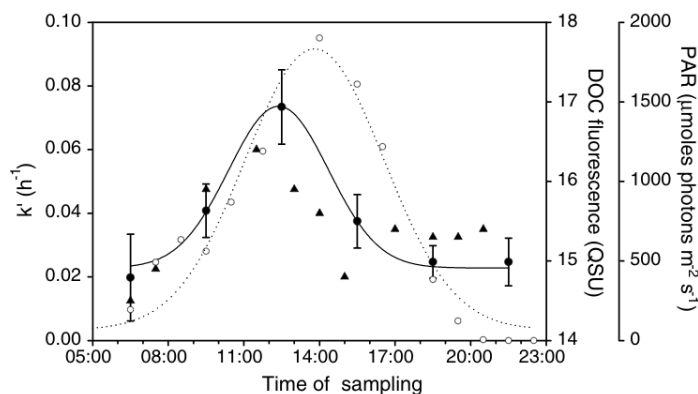


Fig. 2. Diel variations in oxidation rates of Hg^0 (k' , dark circles), DOC fluorescence in lake Croche water (dark triangles), and photosynthetically active radiation (PAR, $\lambda = 400$ – 700 nm , open circles) observed on July 23, 2003. Error bars represent SE.

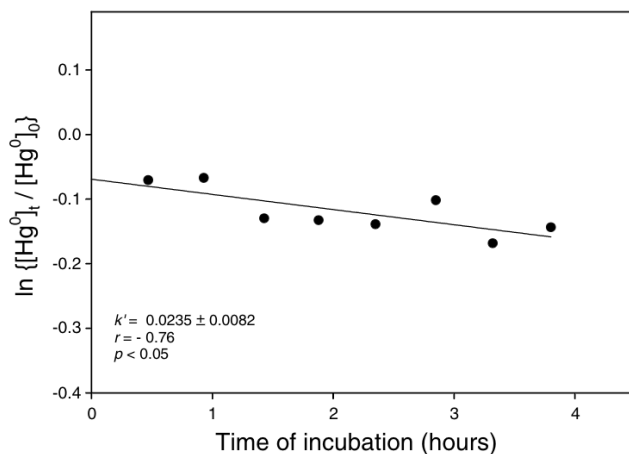


Fig. 3. Hg^0 oxidation in the dark in subsurface water samples from Lake Croche collected at 23:00 on July 22, 2003 and incubated in the dark.

in DGM concentrations in freshwater previously exposed to sunlight of higher intensity than in the same water exposed to sunlight of lower intensity.

DGM concentrations at the beginning of the incubations ranged from 59 to 79 pg l^{-1} (average = 71.8 pg l^{-1}) and did not vary significantly among the different times of sampling, except for DGM concentrations in water collected at 6:30 AM, which was significantly lower. Thus, the observed diel variations in the rate of Hg^0 oxidation are probably more a function of the light intensity and availability of photooxidants than of the amount of substrate.

Decreases in DGM concentrations in the dark following water photoexposure can be attributed to photo-induced generation of oxidants followed by continuous chemical reaction in dark. The similar diurnal dynamics of k^0 and DOC fluorescence (Fig. 2, $r = +0.80$, $p = 0.0575$) suggests a participation of DOC in the Hg^0 oxidation process (Garcia et al., in press). Indeed, the absorption of light by chromophoric DOC can yield photoreactive intermediates and is often followed by losses of DOC fluorescence due to degradation of the chromophores (Del Vecchio and Blough, 2002). These intermediates include excited triplet states of DOC chromophores or DOC-derived radicals, such as hydroxyl ($\cdot\text{OH}$), superoxide ($\cdot\text{O}_2^-$) and hydrogen peroxide (H_2O_2) (Zepp et al., 1981; Leifer, 1988), which have been identified as potential Hg^0 oxidants (Magalhães and Tu-bino, 1995; Lin and Pehkonen, 1999; Lalonde et al., 2004).

3.2. Relative importance of photooxidation and photoreduction

Experiments were conducted to assess the importance of Hg photoinduced oxidation relative to photoreduction at different periods of the day. Variations in DGM estimated for the dark and light treatments at different sampling periods are shown in Fig. 4. Significant decreases in DGM concentrations over time (from 3 to 29 pg l h^{-1}) were observed in samples kept in the dark, in all sampling periods. The greatest decrease was observed in samples collected at 12:50. At this period, the oxidation in the dark was equivalent to 77% of the net production of DGM under sunlight exposure. A decrease in DGM levels (6 pg l h^{-1}) was also noticed in samples from the light treatment collected at dusk (at 19:00). This decrease corresponded to approximately half of the DGM decrease observed in the dark during the same period. In all remaining light exposed samples, a DGM production occurred, varying from 28 to 43 pg l h^{-1} . On

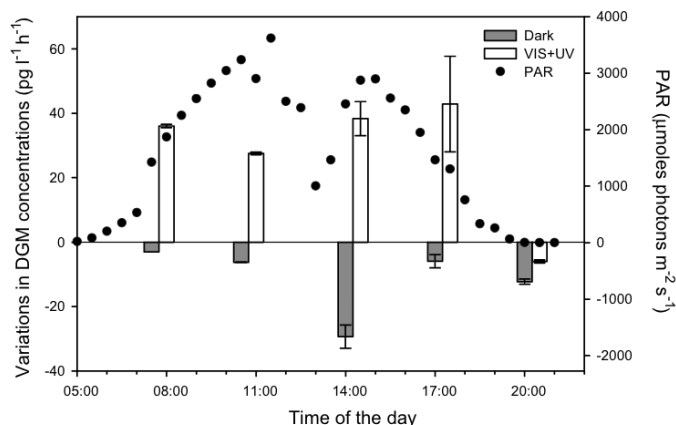


Fig. 4. Variations in DGM concentrations in subsurface water samples from Lake Croche collected at 6:20, 9:20, 12:50, 16:00 and 19:00 on July 25, 2003, and incubated in the dark or under the full spectrum of solar radiation. Each value represents the mean \pm SD based on three replicates.

the whole, these results indicate that in the dark only Hg^0 oxidation is observed in freshwater

In sunlight, oxidation and reduction of Hg may occur simultaneously, but the leading process seems to depend on the light intensity: at higher solar irradiance DGM production overcomes oxidation, but as sunlight energy weakens at cloudy times or at sunset oxidation prevails over reduction. This phenomenon has also recently been observed in snow (Poulain et al., 2004b).

This study demonstrates the occurrence of photoinduced oxidation of Hg^0 in surface freshwater kept in closed systems at natural DGM concentrations and light exposure. However, even at its maximum, the observed photoinduced oxidation seemingly proceeded slower than the concurrent DGM photoproduction. In open surface freshwater, Hg(II) reduction is especially important to Hg cycling due to the evasion of the produced DGM to the atmosphere, particularly on windy summer days. These findings contrast with those for saline waters (Lalonde et al., 2001, 2004), where loss of DGM by photo-oxidation is often more important than volatilization of Hg^0 from the water column. However, at night, Hg^0 oxidation is the dominant process in freshwater and it may replenish the pool of Hg(II) available for methylation. Furthermore, deeper in the water column of a lake, where Hg^0 production is triggered by biological processes rather than solely by light (Siciliano et al., 2003; Poulain et al., 2004a), dark oxidation can be a significant process.

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