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Dissolved Gaseous Mercury Concentrations and Mercury Volatilization in a Frozen Freshwater Fluvial Lake

N. J. O'DRISCOLL,^{*,†} L. POISSANT,[‡]
J. CANÁRIO,^{‡,§} AND D. R. S. LEAN^{||}

Department of Earth & Environmental Science, Room LL33
K.C. Irving Environmental Science Center, Acadia University,
Wolfville, Nova Scotia, B4P 2R6, Centre St-Laurent, Aquatic
Ecosystem Protection Research Division, Water Science and
Technology Directorate Science and Technology Branch,
Environment Canada, 105 rue McGill, 7e étage (Youville) H2Y
2E7, Canada, Instituto Nacional de Recursos Biológicos,
IPIMAR, Av. Brasília, 1449006 Lisboa, Portugal, and Biology
Department, Faculty of Science, University of Ottawa, P.O.
Box 450, Station A, Ottawa, Ontario, Canada, K1N 6N5

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In situ mesocosm experiments were performed to examine dissolved gaseous mercury (DGM), mercury volatilization, and sediment interactions in a frozen freshwater fluvial lake (Lake St. Louis, Beauharnois, QC). Two large in situ mesocosm cylinders, one open-bottomed and one close-bottomed (no sediment diffusion), were used to isolate the water column and minimize advection. Mercury volatilization over the closed-bottom mesocosm did not display a diurnal pattern and was low (mean = $-0.02 \text{ ng m}^{-2} \text{ h}^{-1}$, SD = 0.28, $n = 71$). Mercury volatilization over the open-bottom mesocosm was also low (mean = $0.24 \text{ ng m}^{-2} \text{ h}^{-1}$, SD = 0.08, $n = 96$) however a diurnal pattern was observed. Low and constant concentrations of DGM were observed in surface water in both the open-bottomed and close-bottomed mesocosms (combined mean = 27.6 pg L^{-1} , SD = 7.2, $n = 26$). Mercury volatilization was significantly correlated with solar radiation in both the close-bottomed (Pearson correlation = 0.33, significance = 0.005) and open-bottomed (Pearson correlation = 0.52, significance = 0.001) mesocosms. However, DGM and mercury volatilization were not significantly correlated (at the 95% level) in either of the mesocosms (significance = 0.09 in the closed mesocosm and significance = 0.9 in the open mesocosm). DGM concentrations decreased with depth (from 62 to 30 pg L^{-1}) in the close-bottomed mesocosm but increased with depth (from 30 to 70 pg L^{-1}) in the open-bottomed mesocosm suggesting a sediment source. DGM concentrations were found to be high in samples of ice melt (mean 73.6 pg L^{-1} , SD = 18.9, $n = 6$) and snowmelt (mean 368.2 pg L^{-1} , SD = 115.8, $n = 4$). These results suggest that sediment diffusion of mercury and melting snow and ice

are important to DGM dynamics in frozen Lake St. Louis. These processes may also explain the lack of significant correlations observed in the DGM and mercury volatilization data.

Introduction

Dissolved gaseous mercury (DGM), or dissolved elemental mercury, is the volatile form of mercury in water. The formation and volatilization of DGM from freshwaters is important, as it is a mechanism by which water bodies may naturally reduce their mercury burden (1). Several researchers have demonstrated that volatilization is a significant part of the mercury cycle. Rolffhus and Fitzgerald (2) found that mercury volatilization from Long Island Sound, New York, was equivalent to 35% of total annual mercury inputs to the system, and studies on the Great Lakes (Canada–United States) show that mercury volatilization is equivalent to as much as 50% of the total mercury inputs (3, 4). Recent observations by the METAALICUS research network found that mercury additions to a lake surface are quickly reduced and volatilized to the atmosphere (38–59% after eight weeks) while a portion of the remaining mercury is efficiently methylated and incorporated into the food web (5).

Recent work by O'Driscoll et al. (6) has highlighted the importance of understanding DGM distribution with depth in the water column when modeling volatilization. While there is a wealth of published DGM data for summer sampling (e.g., 7, 8), there are only a few recent publications (e.g., 9, 11) examining the role of ice and snow cover on DGM dynamics in freshwaters. Research on marine and freshwater ice has shown that UVB, UVA, and visible radiation can substantially penetrate 0.5–2 m of ice cover (11, 12). Although solar radiation is reduced, mercury photoreduction will still occur near the ice–water interface in most lakes. With volatilization limited by ice cover, DGM may accumulate during the winter months. However, recent research by Poulain et al. (13) found that winter concentrations of DGM were 10 times less than summer DGM concentrations in Lake 658 at the Experimental Lakes Area (ELA). Similarly, in a 12 month field study of Cane Creek Lake (Cookeville, TN) Zhang et al. (9) observed DGM concentrations followed the monthly mean solar radiation intensity with highest DGM concentrations in July (40.8 pg L^{-1}) and lowest in December (14.2 pg L^{-1}).

To model mercury distribution on a seasonal basis more research is required to determine the factors affecting the vertical distribution of DGM in temperate freshwaters with ice cover. DGM vertical distribution is affected by a number of variables including solar attenuation, mercury volatilization, photoreduction/photo-oxidation kinetics, sediment diffusion, and physical mixing processes. Depth profiles in Ontario lakes have shown that DGM concentrations often increase when approaching the lake bottom (14). Similar small peaks in DGM (60.6 pg L^{-1}) have been observed by Poulain et al. (13) near the sediment–water interface in Lake 658 at the ELA. However, recent work in the St. Lawrence River did not find any evidence of increased DGM near sediments (6). Here we quantify DGM distribution and volatilization from a frozen freshwater fluvial lake (Lake St. Louis, Beauharnois, QC) with elevated concentrations of total mercury in sediment. We test the following hypotheses: (i) higher DGM concentrations will exist near the ice–water interface as compared with DGM at depth; (ii) DGM at the ice surface interface will follow a diurnal pattern; (iii) diffusion of DGM from contaminated sediments may influence DGM

* Corresponding author phone: 902-585-1679; fax: 902-585-1034; e-mail: nelson.odriscoll@acadiau.ca.

[†] Acadia University.

[‡] Environment Canada.

[§] Instituto Nacional de Recursos Biológicos, IPIMAR.

^{||} University of Ottawa.

gradients and water-to-air volatilization rates; and (iv) snowmelt and ice melt are significant in the DGM dynamics of a frozen freshwater lake.

Experimental Section

Analysis Site and Mesocosm Treatments. Field work was performed during February 5–8, 2007 on Lake St. Louis, a widening of the St. Lawrence River near Beauharnois, Quebec (45°19.06' N; 73°52.62') (Figure SI-1 in the Supporting Information). This site is well-known for its sediment mercury contamination (15). A small trailer near shore was used as a mobile laboratory to maintain the analytical equipment at 20 °C. A motorized auger was used to make a series of circular holes in the ice (~25 cm diameter, ice depth of ~50 cm) which were then widened to the diameter of the mesocosm (~100 cm) using a chisel. A separate hole was made approximately 5 m from the mesocosm hole for a reference site for mercury volatilization. The mesocosms consisted of large high-density polyethylene plastic cylinders (91.5 cm diameter, ~142.3 cm height) with 8 holes (~12.7 cm diameter) cut symmetrically into the sides to effectively stop advection but to allow interaction with the water column. One mesocosm had a closed bottom to reduce sediment interactions while the other mesocosm was open-bottomed. The mesocosms were level with the ice surface at the top of the water column and extended to approximately 20 cm above the sediment surface (total lake depth of 170 cm). As such, the open-bottomed mesocosm was exposed to a larger surface area of sediment.

Mercury Flux Analysis. Water-to-air flux of mercury over each of the mesocosms and the reference hole was measured using a floating Teflon dynamic flux chamber with a Tekran 2537A gaseous mercury monitor as described by Poissant and Casimir (16) and Poissant et al. (17, 18). Since we had a single flux chamber mercury volatilization readings could not be taken simultaneously over each mesocosm. As such flux measurements were taken for a minimum of 24 h over the reference hole and each of the mesocosms in series. Air was sampled from the chamber to the Tekran through a 15 m long 1/4 in. Teflon line which was heated and insulated. The chamber consisted of a hemispheric stainless steel bowl coated with Teflon. The open area of the chamber (A) was 0.125 m² and its volume was 0.01 m³ (chamber was 20 cm in height). This chamber was previously intercompared with other types of flux chambers during an international study conducted in Reno, Nevada (19, 17).

Sampled air was transported to the Tekran analyzer located inside the trailer via a 15 m heated Teflon tubing line. The time resolution for the flux measurement was 5 min since each inlet and outlet measurement was used in 2 separate flux calculations (before and after the inlet sample) (6). Before deploying the chamber, blanks were determined in the laboratory over an ultraclean Teflon surface. After the system was flushed several times with mercury-free air the laboratory blanks reached the instrumental lowest blank level of ~0.04 ng m² h⁻¹ (2% precision of the Tekran instrument). After which the flux chamber was assembled with an ultraclean Teflon plate and sealed in a clean plastic bag to avoid contamination during transport. The bag and plate were removed immediately prior to use at the site. The chamber was secured to a buoy at the air–water interface, as described in Poissant and Casimir (16) and occupied approximately 80% of the ice-free area in the mesocosm opening.

Following Xiao et al. (20), the mercury flux (ng m⁻² h⁻¹) from the dynamic flux chamber was calculated as follows:

$$F_{Hg} = \frac{[Hg]_o - [Hg]_i}{A} \times Q \quad (1)$$

where $[Hg]_o$ was the outlet air concentration, $[Hg]_i$ was the inlet air concentration into the chamber, and Q was the flow rate into the chamber (0.09 m³ h⁻¹).

DGM Surface Sampling and Analysis. Continuous DGM analysis (21) was not possible due to sample line freezing (even when heated and insulated). Therefore 1 L Teflon containers were filled with surface water just under the ice but within 30 cm from the ice hole opening each hour using clean sampling methodology and analyzed on-site using a discrete sample DGM analysis (21). Samples were sparged in the Teflon sample container using a specially fitted Teflon sparging head, such that samples did not need to be decanted prior to analysis, thereby minimizing volatile mercury loss. Each Tekran 2537A used for this study was calibrated prior to this analysis using the internal mercury permeation calibration source and standard injections of elemental mercury using a Hamilton digital syringe and a Tekran 2505 mercury vapor calibration unit. The analytical system was allowed to warm and stabilize for a minimum of 2 h before readings were recorded for interpretation. Using this method the detection limit for DGM was 4 pg L⁻¹, and the relative standard deviation (RSD) of duplicates ($n = 36$) was 4.0 ± 2.6% (21). The surface water was continuously analyzed for pH, conductivity, oxidation–reduction potential (ORP), temperature, and dissolved oxygen using a Hydrolab MiniSonde 4a. Depth profiles were measured for temperature, conductivity, salinity, total dissolved solids (TDS), ORP, total dissolved gas (TDG), and dissolved oxygen (DO) using a Hydrolab DS5X, DataSonde 5x Multiprobe.

DGM Depth Profiles. Depth profiles of DGM were performed for each treatment (open-bottomed mesocosm, close-bottomed mesocosm, and natural site) at 12:00 and 18:00 to compare midday measurements with night-time measurements. Measurements of incoming visible, UVA, and UVB radiation were not detectable at 18:00. Water was sampled using a trace metal grade Teflon pneumatic pump using compressed ultrahigh-purity argon as the pressure source. Hydrolab readings for water chemistry parameters (pH, total dissolved gas, dissolved oxygen, temperature, oxidation reduction potential) were measured simultaneously. Once all depths were sampled, the samples were analyzed in random order for DGM on-site and the water was stored in 1 L Teflon bottles kept in the dark prior to analysis. Therefore there was a maximum storage time of 10 h for the final sample from each profile. Previous analyses of DGM have shown that in general <10% standard deviation can be expected on replicated batch samples. In addition, O'Driscoll et al. (21) found that continuous DGM analysis was within 4.7% of discrete batch DGM analysis when a series of triplicate samples was compared. While triplicate analysis of DGM was not possible given the time constraints on sample analysis we have included a 10% error representing the likely maximum analytical error on the DGM analysis. Triplicate samples were also collected at the same time in 50 mL polypropylene centrifuge tubes for the analysis of total mercury and dissolved organic carbon (DOC). Samples were filtered through a 0.45 μm filter and preserved with 0.5% BrCl for total mercury analysis (22), or alternatively frozen for DOC analysis.

Samples for total mercury were analyzed using reduction with stannous chloride and cold vapor atomic fluorescence spectroscopy analysis using a Tekran 2600 instrument. Dissolved organic carbon was measured on samples filtered through a 0.45 μm filter and analyzed by wet chemical oxidation and infrared analysis of carbon dioxide using an OI Analytical TOC analyzer.

DGM in Ice Melt and Snow Melt. The surface snowpack was sampled using clean techniques and 2 L Teflon containers within ~20 m of the experimental site, but away from potential sources of disturbance. Ice samples were also

collected from ice chippings around the mesocosm hole. All ice and snow samples were stored in the dark at room temperature in order to melt the samples. Once melted, the samples were decanted into the Teflon sparger previously described and analyzed for DGM.

Meteorological Variables. Several environmental parameters were continuously measured at the site. Air temperature (T_{air}) and relative humidity (RH) were measured at 1.8 m height above the ice surface by using HMP35 humidity/temperature probes (T_{air} accuracy ± 0.2 °C; RH accuracy $\pm 0.04\%$; Campbell Scientific). Water temperature was monitored using a 107B probe (accuracy 0.2 °C, Campbell Scientific). Net radiation (NR) for both short wave and long wave was recorded by using a Q-7.1 net radiometer (accuracy $\pm 4.3\%$, Campbell Scientific) at 1.8 m height. Wind speed (accuracy $\pm 2\%$) and direction (accuracy 5%) were measured by using an R.M. Young anemometer (Young Scientific) at 2.0 m height. Readings of incoming ultraviolet radiation (UVA 320–400 nm and UVB 280–320 nm) and visible radiation (400–700 nm) were measured every hour using Goldilux GUYA-1L and GUVB-1L equipment.

Results and Discussion

DGM in Surface Water, Ice Melt, and Snow Melt. Low concentrations of DGM were measured at the ice–water interface (mean = 27.6 pg L⁻¹, SD = 7.2 , $n = 26$) with no diurnal pattern observed in either mesocosm. It should be noted that the ice–water interface sampled was very close to the experimental hole and as such may not entirely represent an undisturbed ice–water interface. Diurnal patterns in surface DGM concentrations have been observed during the summer in many freshwater lakes and rivers with DGM concentrations generally ranging between 20 and 100 pg L⁻¹ (6–8, 23). Previous summer DGM concentrations in surface water in the St. Lawrence River near Cornwall, Ontario are 2–4 times higher (60.4 and 134 pg L⁻¹) than mean values measured during this study (6, 23). Lower DGM values in winter have been reported by several researchers. Poulain et al. (13) working in Lake 658 at the Experimental Lakes Area (ELA) found that winter concentrations of DGM were 10 times less than summer DGM concentrations. Similarly, Zhang et al. (9) observed DGM concentrations were lowest in December (14.2 pg L⁻¹) and highest in July (40.8 pg L⁻¹) in a 12 month field study of Cane Creek Lake (Cookeville, TN). This suggests that the low DGM values measured in this winter study are consistent with those in the published literature.

The lack of a diurnal DGM pattern at the ice–water interface of Lake St. Louis may in part represent the inability of DGM to volatilize through the overlying ice cover, however with no volatilization an increase in DGM concentrations would be expected. It is possible that sampling in close proximity to the mesocosm hole may have affected these results. However in our previous research open lake surfaces exhibit a diurnal pattern in DGM concentrations. The low and consistent concentrations of DGM measured at the ice–water interface suggest that either DGM is redistributed through the water column or that photo-oxidation is in balance with photoreduction. Lalonde et al. (24) have previously shown that abiotic photo-oxidation may balance photoreduction in some freshwaters. Siciliano et al. (25) concluded that microbes can significantly reduce and oxidize mercury in fresh water, therefore it is possible biotic oxidation mechanisms may also be balancing mercury reduction at this site. However, biotic oxidation is likely less important at these lower temperatures.

DGM concentrations were found to be substantially higher in samples of ice melt (mean = 73.6 pg L⁻¹, SD = 18.9 , $n = 6$) and snowmelt (mean = 368.2 pg L⁻¹, SD = 115.8 , $n = 4$) than in surface water, suggesting that ice melt may be very important to DGM dynamics at the ice–water interface.

Several researchers have examined mercury deposition and volatilization from snow. Lalonde et al. (26) observed that mercury deposited in snow may be rapidly volatilized to the atmosphere. Poulain et al. (27) found that significant losses occur from the snowpack prior to snowmelt. The amount of total mercury quantified in snow is widely variable, and few researchers have measured DGM concentrations in the melted samples (Table SI-1). We measured concentrations of dissolved gaseous mercury in melted ice (mean = 73.6 pg L⁻¹) and snow (mean = 368.2 pg L⁻¹) that were much higher than levels measured in surface water (mean = 27.6 pg L⁻¹). With total mercury concentrations in ice and snow of 6.8 ng L⁻¹ and 17.6 ng L⁻¹, respectively, the % of total mercury as DGM ranged between 1.0 and 3.0% (Table SI-1). This reservoir of DGM in snow and ice represents an important pool of volatile mercury which may be released during warming periods to surface water where it would be available for volatilization. Snow melt within the snowpack would be less likely to volatilize to the atmosphere due to reduced interaction with wind.

Previously reported mean total mercury concentrations in snow range between 0.5 and 6.18 ng L⁻¹ (Table SI-1) for many northern and arctic sites with highest concentrations ranging between 24.6 and 31.3 ng L⁻¹ in some high arctic sites. The values in this study are over twice the total mercury concentration in many arctic snow samples. The reason for this is unclear but may be related to increased ultraviolet irradiation intensity and duration in the arctic snowpack which may result in increased mercury photoreduction and losses to the atmosphere. It also may be related to chemical characteristics of the snow that may affect mercury reduction efficiencies.

Previous research suggests that dissolved organic matter is necessary for the abiotic photo reduction of mercury in freshwater systems (28) and this may be facilitated by iron-mediated processes (30), however less is known about the mechanisms of mercury photo reduction in rain and snow. Research by Van Loon et al. (31) found that the aqueous mercuric ion can be reduced by sulfite in the atmosphere. Mercury reduction was found to increase with increasing temperature. We speculate that reduction of mercury by sulfite either in the atmosphere or after deposition to the snowpack may partially explain the presence of reduced mercury. In addition, several researchers have found that chloride concentration is negatively related to mercury reduction in temperate and Arctic snow packs and Arctic meltwater ponds (26, 27, 29). The high concentrations of DGM in snow and ice melt observed in this study may partially be due to low concentrations of chloride in snowmelt and thus the increased availability of photoreducible mercury.

DGM Depth Profiles. Many researchers have observed photoproduction of DGM at the surface of freshwater lakes in the summer (e.g., refs 7, 8, 28); however DGM photoproduction in a frozen lake is less well-known. Surface DGM production was clearly observed in the daytime depth profiles of frozen Lake St. Louis (Figure 1) however no diurnal pattern was observed. As previously mentioned, DGM surface values (mean 27.6 pg L⁻¹, SD = 7.2 , $n = 26$) are 2–4 times lower than summer DGM measurements in samples from the St. Lawrence River near Cornwall (6, 23). DGM production may be lower due to increased attenuation of solar radiation by snow and ice cover. Photoreduction of mercury has been shown to be driven primarily by ultraviolet portions of solar radiation (32). Belzile et al. (11) examined transmission of solar radiation through 2 m of ice and 0.5 m snow cover on Lake A (Ellesmere Island, Canada). The authors found that radiation transmission increased substantially with removal of snow cover (from 0.45 to 5.85% for PAR, and from 0.4% to 6.3% for UV radiation). Since some patchy snow cover was present on Lake St. Louis we can assume that levels of UV

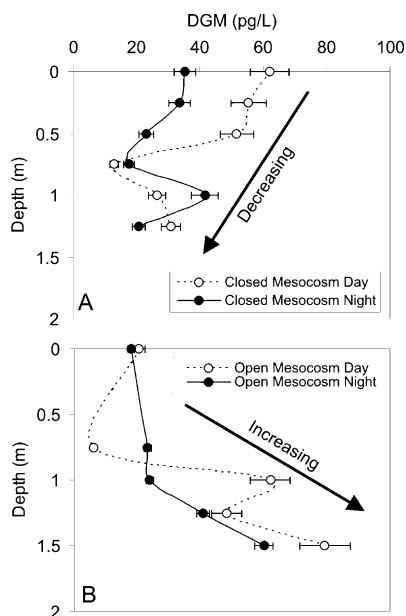


FIGURE 1. Daytime and night time dissolved gaseous mercury depth profiles in open-bottomed mesocosm (A) and close-bottomed mesocosm (B) in Lake St. Louis.

attenuation are within this range. However, since some radiation is available in the unfrozen water column, DGM photoproduction may occur.

The observed increase in DGM at the top of the water column in the close-bottomed mesocosm (Figure 1a) is consistent with the limited published literature on DGM depth profiles in freshwaters. The increase in DGM in the surface water and may be due to either abiotic photoreduction reactions, microbial reduction process (25), or snowmelt sources of DGM as previously discussed. Poulain et al. (13) performed a depth profile of DGM in late winter (March) under the ice of Lake 658 in ELA. They observed highest winter concentrations of DGM in the top 2 m of the water column and a second DGM peak occurring close to 10 m depth which was attributed to phytoplankton blooms. Siciliano et al. (14) also observed an increase in DGM concentrations in the top of the Lake Ontario water column during summer. Tseng et al. (33) found that vertical profiles of DGM in the ice-free season of a relatively shallow lake (~20 m depth) decreased with depth and were 2–6 times greater in the epilimnion than the hypolimnion in Alaskan Lakes. Although there are very different irradiation intensities and patterns, similar results have been observed in a number of temperate (7, 34) and Arctic lakes (35).

The increasing trend in the open-bottomed mesocosm (Figure 1b) suggests that sediment diffusion or near sediment microbial reduction may be important in this system. This is also supported by an increase in total mercury concentrations (from 0.4 to 1.1 ng L⁻¹) in the open-bottomed mesocosm when approaching the sediment–water interface (Figure SI-2). Siciliano et al. (14) observed similar increases in DGM when approaching the sediment–water interface in Jack's Lake and Lake Ontario. It is unclear in this study whether the increase in DGM was due to abiotic or biotic reduction mechanisms and whether the DGM was formed in sediment or at the sediment–water interface. Very little is known about mercury dynamics at the sediment–water interface. Poulain et al. (13) observed peaks of DGM at depth related to mixotrophs within the water column. It is possible that mixotrophs are important to mercury reduction at the sediment–water interface. Previous work on the St. Lawrence River near Cornwall did not find any evidence of increased DGM near sediment (6). Therefore it is also unclear whether this is a spatially or seasonally limited occurrence. Longer

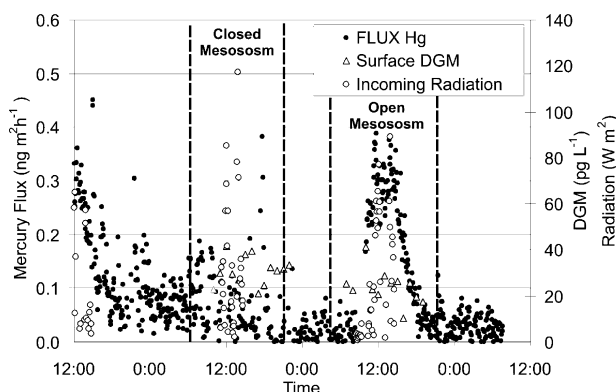


FIGURE 2. Incoming solar radiation, dissolved gaseous mercury concentration (DGM), and mercury volatilization (flux) over a 72 h period in the surface water of Lake St. Louis. No correlations are observed in the closed mesocosm, while solar radiation and mercury volatilization are correlated in the open mesocosm but DGM is not.

term replication of these measurements would be a useful future addition to determine seasonal patterns of DGM depth profiles.

Increasing dissolved organic carbon concentration has been shown to increase the photoreduction rate of mercury in the surface of freshwaters (28). However, dissolved organic carbon and dissolved inorganic carbon profiles did not change significantly with depth in water column (mean DOC = 2.3 mg L⁻¹, SD = 0.09, mean DIC = 21.2 mg L⁻¹, SD = 0.22, $n = 23$). Recent work by Poissant et al. (36) on the St. Lawrence River found that mercury released from the bubbling of sediment gas was negligible, however significant amounts of methane gas was released. Recent work by Telmer (37) in the Amazon River suggests that in some areas substantial mercury may be associated with methane gas release from sediments. Total dissolved gas (as measured by Hydrolab multiprobe) was observed to increase with depth at this site from 714 to 721 mmHg (Figure SI-3) suggesting that the sediments are a source of dissolved gas (such as methane). In addition, there is a small increase in the oxidation reduction potential with depth (Figure SI-3) (from 480 to 476 over 160 cm) which would likely have negligible effects on chemical mercury reduction. It is possible that the physical act of methane bubbling from sediments may enhance the release of dissolved gaseous mercury from sediment pore waters to the sediment–water interface.

DGM and Mercury Volatilization. Mercury volatilization was measured over both in situ mesocosms as well as over the ice surface and a reference hole. Mercury volatilization was low and relatively constant over ice (mean = 0.23 ng m⁻² h⁻¹, SD = 0.02, $n = 164$), the reference hole (mean = 0.08 ng m⁻² h⁻¹, SD = 0.09, $n = 227$), and over the close-bottomed cylinder (mean = -0.02 ng m⁻² h⁻¹, SD = 0.28, $n = 71$). Mercury volatilization over the open-bottomed cylinder was also observed to be low (mean = 0.24 ng m⁻² h⁻¹, SD = 0.08, $n = 96$) however a diurnal pattern was observed (Figure 2). Poissant et al. (38) measured a median mercury volatilization of 0.31 ng m⁻² h⁻¹ at St. Anicet (Lake St. Francis) on the upper St. Lawrence River during summer, and the mean mercury volatilization values measured in this study during winter are in a similar range. However, mercury concentrations in Lake St. Louis Hg in sediments are much larger (>100,000 ng g⁻¹) than those measured in Lake St. Francis sediments (<300 ng g⁻¹) (15). This suggests that, while we do observe increases in DGM and total mercury with depth in the water, the high concentrations of total mercury in the sediments at the Lake St. Louis site are not resulting in increased mercury volatilization in the winter relative to summer readings from other sites on the St. Lawrence River.

Future summer readings of mercury flux at this site may indicate if the contaminated sediments result in significantly higher flux during the ice-free season.

Mercury water-to-air flux was significantly but weakly correlated with solar radiation in both the close-bottomed (Pearson correlation = 0.33, significance = 0.005) and open-bottomed (Pearson correlation = 0.52, significance = 0.001) mesocosms. Cross-correlation analysis between solar radiation and mercury volatilization indicated that maximum correlations occurred at 0 min lag time \pm 20 min error for both mesocosms. Previous summer measurements of lag time of the St. Lawrence River showed a 55–145 min lag time between DGM formation and mercury volatilization (6). This lag time was attributed to DGM formation at depth and subsequent diffusion to surface water. The lack of a lag in this experiment suggests that DGM is more efficiently transported from depth to surface water at this site, or that snow and ice melt are a significant source at the water–air boundary.

No significant (95% levels) correlations were observed between the 95% level between DGM in surface water and mercury volatilization in either of the mesocosms (significance = 0.09 in the closed mesocosm and significance = 0.9 in the open mesocosm). This is surprising as there is a wealth of publications describing experimental (8, 38) and modeled (38) research which has observed a relationship between DGM and mercury volatilization.

There are several possible explanations for the observed lack of relationship between DGM and mercury volatilization. One hypothesis is that wind disturbances of the surface micro layer were dominating the mercury volatilization dynamics. Wind speed has been suggested by many researchers to be a critical factor affecting volatilization (8). While volatilization was substantially greater over the open-bottomed mesocosm (Figure 2), wind speed was not significantly different (open-bottomed mesocosm mean wind speed = 4.6 m s⁻¹, SD = 0.9, *n* = 90; close-bottomed mesocosm mean wind speed = 4.4 m s⁻¹, SD = 0.7, *n* = 97) suggesting that wind speed did not significantly affect mercury flux dynamics. It is likely that wind was a less important variable affecting mercury flux due to the amount of ice cover limiting disturbance of the water surface and the use of a dynamic flux chamber which covered ~80% of the ice-free mesocosm opening. However we would also note that this experimental design likely provides conditions similar to early winter and late spring ice coverage when surface waters are ~80% covered and insulated from wind effects.

Another hypothesis is that DGM losses due to volatilization in surface water are balanced by other inputs of DGM from sources such as near sediment production and snow and ice melt. This research confirms that sediment and snow sources of DGM may, in part, explain the lack of diurnal variation in DGM and the lack of correlation to volatilization dynamics observed. However more research is required to determine how these processes may affect mercury fate in a wide range of freshwaters with variations in ice cover and sediment interactions.

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Supporting Information Available

Position of sampling site on Lake St. Louis near Beauharnois, Quebec (Figure SI-1); total mercury concentrations with depth in the closed- and open-bottomed mesocosms (Figure

SI-2); total dissolved gas pressure and oxidation–reduction potential with depth in the natural water column (Figure SI-3); total mercury and dissolved gaseous mercury concentrations reported for snow and ice samples (Table SI-1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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