Mercury dynamics and transport in two Adirondack lakes

Pranesh Selvendiran,[1] *Charles T. Driscoll, and Mario R. Montesdeoca*
Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York 13244

Hyun-Deok Choi and Thomas M. Holsen
Department of Civil and Environmental Engineering, Clarkson University, Potsdam, New York 13699-5710

Abstract

We investigated the chemistry and fluxes of mercury (Hg) species for two Adirondack lakes with contrasting landscape, physical, and chemical attributes. Samples were collected monthly at the lake inlets and outlets over 2 yr, and evasion of elemental Hg was measured at one lake (Arbutus). Concentrations of total Hg (THg) and methyl Hg (MeHg) in watershed runoff were highly variable throughout the year, increasing markedly during summer months. The proportion of THg as MeHg ranged from <5% at Arbutus Lake up to 10% at Sunday Lake. Concentrations of Hg species increased with increases in dissolved organic carbon concentrations and percentage wetland coverage. The estimated rate of volatilization loss of elemental mercury (Hg°) from Arbutus Lake surface (7.8 μg m^{-2} yr^{-1}) was comparable to the rate of direct atmospheric Hg deposition to the lake surface (8.6 μg m^{-2} yr^{-1}). Dry deposition to Arbutus Lake amounted to ca. 26% of total wet THg deposition. Hydraulic residence time (HRT) played a critical role in controlling Hg dynamics in the lakes. Negligible removal of THg inputs was observed at Sunday Lake, which has a short HRT (0.02 yr), compared with approximately 60% removal at Arbutus Lake, which has a longer HRT (0.6 yr). This pattern of increasing net Hg retention in lakes with increasing HRT was consistent with other mass balance studies in the literature. Both Arbutus and Sunday lakes were net sinks of MeHg.

Lakes draining forested glaciated regions of North America and Europe have been affected by atmospheric Hg deposition (Meili et al. 1991; Kamman et al. 2005). Watershed attributes strongly influence the role of lakes in the transport and transformations of Hg. In remote lake districts, atmospheric Hg deposition is the major source of Hg inputs (Fitzgerald et al. 1998). Hg deposition to watersheds is greatly enhanced by forest cover (Rea et al. 2001). Wetlands also play a critical role in Hg dynamics because of reducing conditions that facilitate the conversion of ionic Hg (Hg^{2+}) to methyl Hg (MeHg), and enhanced transport of Hg species to downstream aquatic ecosystems through dissolved organic carbon (DOC) production and binding (Driscoll et al. 1998). Following transport to lake ecosystems, Hg can be removed by deposition to lake sediments, reduction and volatilization to the atmosphere, or export from the outlet. Ionic Hg entering the lake can be methylated in the water column or sediments, and inputs of MeHg can be removed by oxidative or reductive demethylation (Mason and Benoit 2003). Autochthonous or allochthonous MeHg strongly bioaccumulates along the aquatic food chain, resulting in potential exposure to humans and wildlife (Evers et al. 2007).

A critical characteristic that influences the role of lakes in the dynamics of Hg across the landscape is the watershed area to lake surface area ratio. The watershed area to lake surface area ratio controls the relative hydrologic inputs to the lake and the associated hydraulic residence time (HRT). The biogeochemical processing of many elements is linked to HRT (Kelly et al. 1987). Our working hypothesis is that HRT is an important controller of Hg processes in lake ecosystems and ultimately of the exposure of aquatic biota to this element.

Volatilization of elemental mercury (Hg°) is an important mechanism for its removal from ecosystems. Measurements of volatilization of Hg° from remote lakes range from 7% to >100% of total Hg (THg) deposition (Watras et al. 1994; Kotnik et al. 2002). Therefore, Hg° volatilization represents an important component of the Hg budget of lakes. Sunlight-induced Hg reduction appears to be the primary process driving the production of dissolved gaseous Hg (DGM) in lakes and its subsequent loss to the atmosphere (Amyot et al. 1994; O'Driscoll et al. 2003a). Several proposed mechanisms include direct photolysis of Hg^{2+} to Hg° (Amyot et al. 1994), including photosensitizing of Fe^{3+} complexes (Zhang and Lindberg 2001; Ababneh et al. 2006), sulfite complexes (Van Loon et al. 2000), and DOC and humic substances (Xiao et al. 1995), and reduction of Hg^{2+} involving oxygen radicals such as O$_2^{\bullet-}$, HO$^{\bullet}$, and H$_2$O$_2$ (Dommergue et al. 2003). Photodecomposition of MeHg to Hg° has also been suggested (Tossell 1998).

The objective of this study was to assess the role of lakes in the transport and transformations of Hg as part of the

forested landscape of the Adirondack region of New York. Detailed measurements of THg and MeHg were made in the inflow and outlets of two drainage lakes with contrasting watershed area, land cover and HRT: Arbutus Lake and Sunday Lake. We conducted mass balances on Hg species for these lakes, and examined how physical and chemical factors influenced the processing of Hg. In order to better understand transport and removal mechanism, we made measurements of Hg° evasion from Arbutus Lake.

This research was conducted at the 3.52-km² Arbutus Lake watershed (ALW) at the Huntington Wildlife Forest (HWF) in the central Adirondack region of New York (43°59′N, 74°14′W) and the 13.4 km² Sunday Lake watershed (SLW) in the western Adirondacks (41°51′N, 75°06′W). The Huntington Forest has long been a focus of biogeochemical studies, notably on sulfur (Mitchell et al. 1998) and nitrogen dynamics (McHale et al. 2004). Sunday Lake is also a site of a previous detailed lake and watershed study of Hg dynamics (Lindeman 1996).

ALW has 4% of its land area as wetlands. The Arbutus Lake outlet is gauged with a V-notch weir, whereas the primary inlet to the lake draining the sub-catchment Archer Creek (1.30 km²) is gauged with an H-flume. Approximately 40% of the flow into Arbutus Lake drains from this catchment. Dominant tree species include American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), eastern hemlock (*Tsuga canadensis* [L.] Carr.), red spruce (*Picea rubens* Sarg.), and balsam fir (*Abies balsamea* [L.] Miller). Upland soils, typically <1 m deep, are largely coarse, loamy, mixed, frigid, Typic Haplorthods in the Becket-Mundal series. The wetland soil type is mainly Greenwood Mucky peat that varies from 1 to 5 m in thickness. The watershed has a mean slope of 11% and a total relief of 225 m (McHale et al. 2004).

Sunday Lake is located about 80 km directly west of Arbutus Lake. SLW is a second-growth northern hardwood forest and has about 20% land cover as wetlands. Forest cover includes 70% deciduous and 30% coniferous second-growth forest. The inlet and outlet at Sunday Lake are equipped with pressure transducers and automatic data loggers to record discharge rates. The dominant tree species include American beech, red spruce, and balsam fir. Other minor trees species include yellow birch (*Betula alleghaniensis* Britt.), red maple (*Acer rubrum* L.), striped maple (*Acer pennsylvanicum* L.), white pine (*Pinus strobus* L.), and eastern hemlock. Upland soils are well drained Spodosols (Typic Haplorthods), with a sandy loam to loamy sand texture. Site features of ALW and SLW are provided in Table 1.

Methods

Monthly precipitation volume and THg concentrations were obtained from the Mercury Deposition Network (site ID NY20) operating at the HWF. Precipitation amounts for Sunday Lake were obtained from Stillwater Reservoir, located approximately 6 km from SLW. Precipitation THg concentrations obtained at the HWF were assumed to be the same for SLW because of the proximity of location and similarity in precipitation patterns (Lindeman 1996). Wet

Table 1. A summary of physical and landscape characteristics of Arbutus and Sunday Lake watersheds in the Adirondacks, New York.

Parameter	Arbutus Lake	Sunday Lake
Precipitation (mm yr^{-1})	1010	1300
Watershed area (km²)	3.52	13.4
% wetland coverage	4	20
Lake surface area (km²)	0.48	0.077
Watershed : lake surface area	7.3	174
Maximum depth (m)	8.4	5.5
Mean depth (m)	3.0	2.5
Hydraulic residence time (yr)	0.60	0.02

deposition fluxes were estimated by multiplying monthly precipitation amounts and THg concentrations.

Total annual dry deposition was estimated as the summation of monthly fluxes of reactive gaseous Hg (RGM) and particulate Hg (HgP). The following model was applied:

$$F_{RGM} = C_{RGM} \times K_a \quad (1a)$$

and

$$F_{HgP} = C_{HgP,f} \times V_{d,f} + C_{HgP,c} \times V_{d,c} \quad (1b)$$

where F_{RGM} is RGM flux in μg m^{-2} yr^{-1}, C_{RGM} is concentrations of RGM in ng m^{-3}, and K_a is the air mass transfer coefficient for RGM in cm s^{-1} (~0.04–1.48 cm s^{-1}; Lai et al. 2007). F_{HgP} is HgP flux in μg m^{-2} yr^{-1} and $V_{d,f}$ and $V_{d,c}$ are the deposition velocity for fine- and coarse-particle Hg respectively in cm s^{-1} (~0.07–0.19 cm s^{-1} for fine-particle and ~0.12–0.30 cm s^{-1} for coarse-particle; Lai et al. 2007). To include the contribution from coarse-particle dry deposition, the HgP coarse-particle concentration was estimated by assuming that it made up 30% of the total HgP concentration (Landis et al. 2002). The concentrations of RGM and HgP were measured with an automated Tekran speciation system at a clearing a short distance from Arbutus Lake as part of upland Hg research at the HWF from June 2006 to May 2007 (H.-D. Choi pers. comm.).

Water samples were collected monthly from August 2004 through July 2006 at the inlets and outlets of Arbutus and Sunday Lakes. Additionally, the lake surface was also sampled at Arbutus Lake. Samples for Hg analyses were collected into acid-cleaned Teflon bottles according to ultraclean trace metal protocols (Method 1669; Environmental Protection Agency [EPA] 1996). A second set of samples was collected for ancillary water chemistry analyses. During sampling, bottles were rinsed thoroughly with site water before collection. After collection, samples were double-bagged, stored in a cooler with ice packs, and transported to the laboratory, where samples were preserved with 0.4% trace metal–grade HCl and stored at 4°C for Hg analysis. A portion of the sample was vacuum-filtered, following clean techniques, through a polyethersulfone filter (0.45 μm) prior to acid preservation for the analyses of dissolved Hg. Filters were assembled in clean

Teflon holders and prerinsed with 500 mL of 1% trace metal–grade hydrochloric acid, followed by 500 mL of deionized water to remove residual acidity.

The major inflow to Arbutus Lake drains an area of 1.35 km², Archer Creek catchment. The primary inflow to Sunday Lake drains an area of 11.83 km². A secondary inflow at Sunday Lake draining a much smaller area (0.90 km²) was also sampled. The entire outflow at Sunday Lake passes through a beaver dam. Outflow samples were collected below the beaver dam.

THg was analyzed via oxidation, purge and trap, and cold vapor atomic fluorescence spectroscopy (CVAFS; EPA 2002; Method 1631, revision E). MeHg was analyzed via distillation, aqueous ethylation, purge and trap, and CVAFS (EPA 2001; Method 1630, modified to 90 mL of sample). The method detection limit is 0.2 ng L^{-1} and 0.02 ng L^{-1} for THg and MeHg, respectively. Ancillary water chemistry was analyzed via standard methods (American Public Health Association, American Water Works Association, and Water Environment Federation 1998) including DOC, the persulfate–ultraviolet oxidation method (5310C); anions, ion chromatography with chemical suppression of eluent conductivity (4110 B); and pH by electrometric method (2320). Base cations and metals were analyzed via inductively coupled plasma mass spectrometry (EPA method 200.8) and pH by electrometric method (2320). Quality assurance was maintained through duplicate sampling, trip, and process blanks; continuous calibration verification (CCV); continuous calibration blank; matrix spike (MS); and matrix spike duplicates (MSD). The recoveries for spikes and standards were well within method guidelines ($\pm 10\%$ on CCV, MS, and MSD) for THg, MeHg, and ancillary chemical analyses. Additional quality control samples such as initial and ongoing precision recovery, instrument detection limit, and second source verification were used to evaluate instrument performance and stability during analysis.

Monthly discharge was used for flux calculations. For non-channelized inflows to the lake, discharge was prorated based on the respective drainage areas at SLW and ALW. Monthly hydrologic fluxes of THg, MeHg, and DOC were estimated as the product of concentrations and discharge rates. Monthly hydrologic and atmospheric fluxes were summed to annual flux rates. In addition to annual fluxes, Hg fluxes were estimated for the growing and nongrowing seasons. The growing season was defined as 01 May–30 September and the nongrowing season as 01 October–30 April. Lake retention coefficient (R) was estimated as follows:

$$R = (Input - Output)/(Input) \tag{2}$$

The retention coefficient represents the proportion of the incoming mass that was removed from the water column either to sedimentation or to the atmosphere. To obtain percentage retention the value of R was multiplied by 100.

DGM measurements at Arbutus Lake—Diurnal measurements of DGM were made only at Arbutus Lake by applying the method described in O'Driscoll et al. (2003*b*).

Concentrations of DGM were measured twice at Arbutus Lake. During summer (July) 2006 only limited DGM measurements were made because of a rainfall event and subsequent instrument malfunction. Detailed diurnal DGM measurements were made continuously over 46 h during fall (September) 2006. A 1.5-liter volumetric glass sparger in series with a Hydrolab Minisonde 4a and a Tekran 2537A elemental Hg analyzer was used to measure DGM in lake water every 5 min. Water was pumped from the lake at a rate of 50 mL min^{-1} into the sparger using a peristaltic pump (Cole Parmer: 7524-40) and 0.64-cm-diameter Teflon tubing. Water was sampled at a depth of 12 cm from the lake surface and at a distance of 15.24 m from the lake shore. The water was passed through the Hydrolab to measure its pH, temperature, oxidation reduction potential (ORP), dissolved oxygen (DO), and specific conductance. A zero-air generator (Tekran Model 1110) was used to supply Hg-free air to the sparger at a flow rate of 1 L min^{-1}. Simultaneous measurements of solar radiation, wind speed, air temperature, and humidity were made using a weather station (Vantage Pro 2 plus). A more complete description of the method is given in O'Driscoll et al. (2003*b*).

In-lake THg retention—Kelly et al. (1987) developed an internal lake process model to estimate mass transfer coefficients for SO_4^{2-} and nitrate (NO_3^-) to explain retention caused by diffusion into lake sediments. We applied the same model to estimate similar mass transfer coefficients for THg in lakes. According to the model:

$$
\begin{aligned}
R_{THg} &= \frac{S_{THg}}{S_{THg} + (Z/HRT)} \quad \text{or} \\
S_{THg} &= \frac{R_{THg} \times (Z/HRT)}{1 - R_{THg}}
\end{aligned}
\tag{3}
$$

where R_{THg} is THg retention (unitless), S_{THg} is mass transfer coefficient (m yr^{-1}), Z is the mean depth of lake (m), and HRT is expressed in years. In this equation, Z/HRT is the height of the water column that is displaced by new water each year and the mass transfer coefficient is the height of the column from which THg is removed each year.

Results

Concentrations of Hg species at Arbutus and Sunday Lakes—Data collected from August 2004 to July 2006 established clear differences in Hg chemistry between Arbutus Lake and Sunday Lake (Table 2). At Arbutus Lake, average annual volume-weighted concentrations of THg and MeHg were higher in the inlet stream (THg, 3.15 ng L^{-1}; MeHg, 0.12 ng L^{-1}) compared to the outlet (THg, 1.93 ng L^{-1}; MeHg, 0.06 ng L^{-1}). At Sunday Lake, mean annual volume-weighted concentration of THg at the inlet (2.91 ng L^{-1}) was only slightly higher than the outlet value (2.84 ng L^{-1}). However, a notable decline in MeHg concentrations was observed at the outlet (0.23 ng L^{-1}) compared to the inlet (0.32 ng L^{-1}). Concentrations of Hg in the dissolved phase represent 83% and 78% of THg at

Table 2. Annual average volume-weighted solute concentrations in drainage waters at Arbutus and Sunday Lakes from August 2004 through July 2006.

Constituents	Arbutus Lake		Sunday Lake	
	Inlet	Outlet	Inlet	Outlet
THg (ng L^{-1})	3.15	1.93	2.91	2.84
THg-F (ng L^{-1})	2.54	1.52	1.90	1.70
% THg dissolved	83	78	66	68
MeHg (ng L^{-1})	0.12	0.06	0.32	0.23
MeHg-F (ng L^{-1})	0.13	0.06	0.29	0.19
% MeHg	5.71	3.86	10.41	8.17
% MeHg dissolved	92	93	86	86
pH	6.0	6.3	5.4	5.3
DOC (mg L^{-1})	6.50	5.08	7.22	7.28
TSS (mg L^{-1})	0.49	1.34	2.27	2.28
SO$_4^{2-}$ (mg L^{-1})	5.58	5.14	4.01	3.97
Cl$^-$ (mg L^{-1})	0.36	0.35	0.27	0.26
F$^-$ (mg L^{-1})	0.11	0.09	0.09	0.09
NO$_3^-$ (mg L^{-1})	0.99	0.35	0.98	0.98
Ca^{2+} (mg L^{-1})	2.24	1.72	0.91	0.91
Mg^{2+} (mg L^{-1})	0.44	0.43	0.27	0.27
Na$^+$ (mg L^{-1})	0.84	0.73	0.76	0.73
K$^+$ (mg L^{-1})	0.21	0.24	0.34	0.36
Mn (μg L^{-1})	8.27	8.37	29.88	35.00
Fe (mg L^{-1})	0.08	0.07	0.45	0.41

THg, total mercury; THg-F, total mercury filtered; MeHg, methyl mercury; MeHg-F, methyl mercury filtered; DOC, dissolved organic carbon; TSS, total suspended solids; SO$_4^{2-}$, sulfate; NO$_3^-$, nitrate.

the inlet and outlet, respectively, at Arbutus Lake. Comparatively higher particulate association of Hg was evident at Sunday Lake, with 66% and 68% of THg occurring in dissolved phase at the inlet and outlet, respectively (Table 2).

Concentrations of DOC declined at the outlet (5.08 mg L^{-1}) compared to the inlet at Arbutus Lake (6.50 mg L^{-1}). Although concentrations of DOC were higher at Sunday Lake, no noticeable change was observed between the lake inlet and outlet. A net export of total suspended solids (TSS) was observed from the Arbutus Lake outlet (1.34 mg L^{-1}) compared to the inlet (0.49 mg L^{-1}). Sunday Lake exhibited no net change in TSS at the inlet and outlet ($\sim$ 2.3 mg L^{-1}). Lower sulfate (SO$_4^{2-}$) concentrations were observed at Sunday Lake compared to Arbutus Lake. At both Sunday and Arbutus Lakes, SO$_4^{2-}$ was the dominant anion, followed by NO$_3^-$, chloride (Cl$^-$), and fluoride (F$^-$) (Table 2). Concentrations of dissolved total manganese (Mn$_T$) and total iron (Fe$_T$) were approximately fivefold and fourfold greater at Sunday Lake than at Arbutus Lake (Table 2). pH at the outlet of Arbutus Lake increased by 0.3 units compared to the inlet (6.0), implying in-lake production of acid-neutralizing capacity and/or losses of CO$_2$ and organic acids, whereas a slight decline in pH was observed at the outlet (5.3) of Sunday Lake compared to the inlet (5.4).

Temporal Hg patterns at Arbutus and Sunday Lakes—Marked temporal variations were observed in THg concentrations at the inlet of Arbutus Lake. Peak
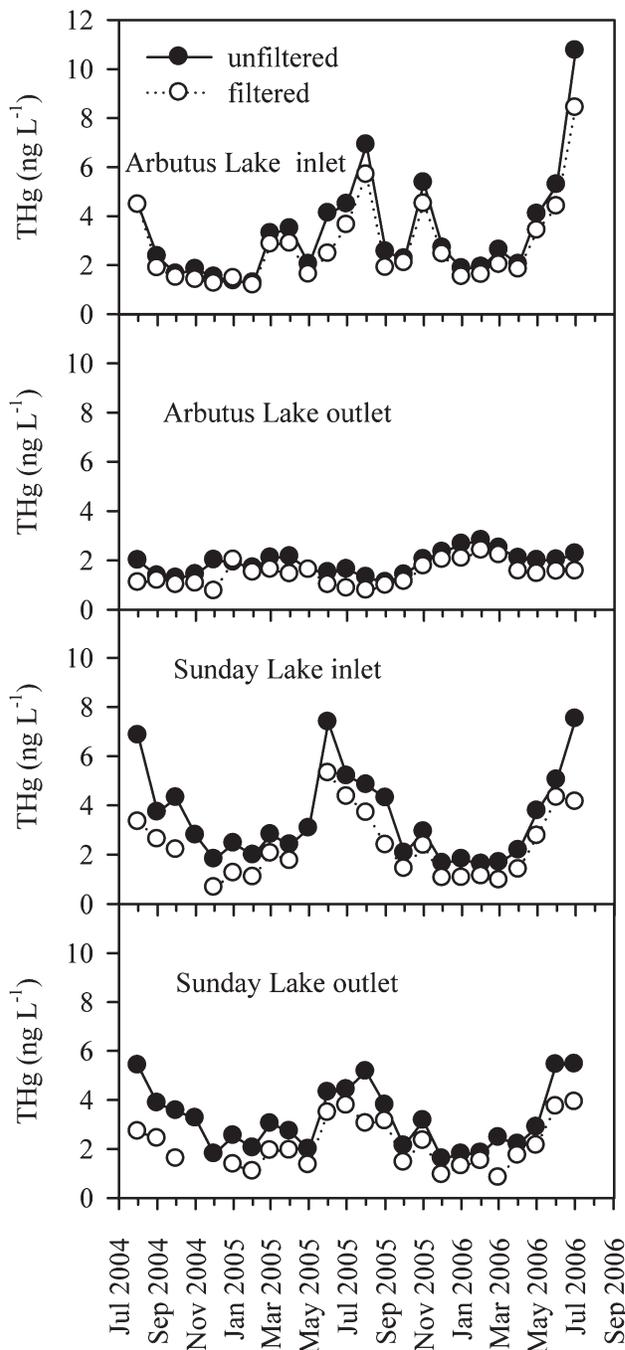

Fig. 1. Temporal patterns in filtered and unfiltered THg concentrations (ng L^{-1}) within the inlet and outlet of Arbutus and Sunday Lakes.

concentrations of THg at the lake inlet occurred during summer months (Fig. 1). Secondary peaks in THg concentrations in the inlet were observed during high-discharge (e.g., November 2005) and snowmelt events (e.g., April 2005, March 2006; Fig. 1). At Arbutus Lake, outlet THg concentrations varied less with no apparent temporal patterns. Also, mean annual volume-weighted THg concentrations were consistently lower at the outlet (1.93 ng L^{-1}) compared to the inlet (3.15 ng L^{-1}), indicat-

ing a net removal of THg within Arbutus Lake. During summer, THg concentrations increased at the Sunday Lake inlet, similar to the Arbutus Lake inlet (Fig. 1). In contrast to Arbutus Lake, the temporal patterns in THg concentrations at the outlet were identical to the inlet at Sunday Lake. Mean annual volume-weighted concentrations of THg at the inlet and outlet were similar (2.91 and 2.84 ng L^{-1}; Table 2), implying limited retention of THg at Sunday Lake.

Temporal patterns of MeHg showed strong variation with season at the inlets of Arbutus and Sunday Lakes. During the cold season (October–May), concentrations of MeHg were low (0.08 and 0.19 ng L^{-1} at Arbutus and Sunday Lakes, respectively). During the warm season (Jun–Sep), concentrations of MeHg at the inlet increased fivefold (0.32 ng L^{-1}) at Arbutus Lake and sixfold at Sunday Lake (0.73 ng L^{-1}). Concentrations of MeHg at the outlet of Arbutus Lake did not show any apparent temporal pattern and declined twofold compared to the inlet (Fig. 2; Table 2). At the Sunday Lake outlet, strong seasonal patterns in MeHg concentrations, similar to those at the inlet, were observed.

Hg relationship with DOC, SO_4^{2-}, and Fe—DOC has been shown to strongly associate with Hg species (Driscoll et al. 1998; Dennis et al. 2005). Markedly high concentrations of THg and MeHg were observed at inlets during the summer months (Figs. 1, 2), coinciding with elevated production of DOC in wetlands (Selvendiran et al. 2008). Combining all surface waters for both lake watersheds, we found statistically significant correlations between DOC and both THg and MeHg ($\alpha = 0.05$; $p < 0.000$; Fig. 3a,b). A relatively higher percentage of wetland coverage at SLW (20%) compared to Arbutus Lake (4%) resulted in elevated DOC, THg, and MeHg concentration at inlet streams to Sunday Lake.

SO_4^{2-} reduction is linked to the production of MeHg (Jeremiason et al. 2006). A significant inverse nonlinear relationship between SO_4^{2-} and MeHg was observed by combining surface water data for Sunday and Arbutus Lakes (Fig. 4a). At Arbutus Lake, where SO_4^{2-} concentrations were greater than 4.5 mg L^{-1}, MeHg concentrations were correspondingly lower. At Sunday Lake, when SO_4^{2-} concentrations decreased <4 mg L^{-1}, a corresponding steep increase in MeHg concentrations was observed.

A linear relationship between Fe$_T$ and MeHg, with varying slopes, was found for Arbutus and Sunday Lakes (Fig. 4b). The presence of dissolved Fe$_T$ in surface waters is likely an indicator of reducing conditions and/or complexation with elevated DOC. Researchers have found that the distribution and mobility of MeHg is coupled with the redox cycling of Fe (Bloom et al. 1999). A linear relation between Fe$_T$ and MeHg may imply the production of MeHg under reducing conditions.

Budget calculations—Average precipitation during the study period (August 2004–July 2006) was similar at Arbutus Lake (1254 mm yr^{-1}) and Sunday Lake (1237 mm yr^{-1}). Direct precipitation contributed about 20% of the water input to Arbutus Lake. Surface runoff from
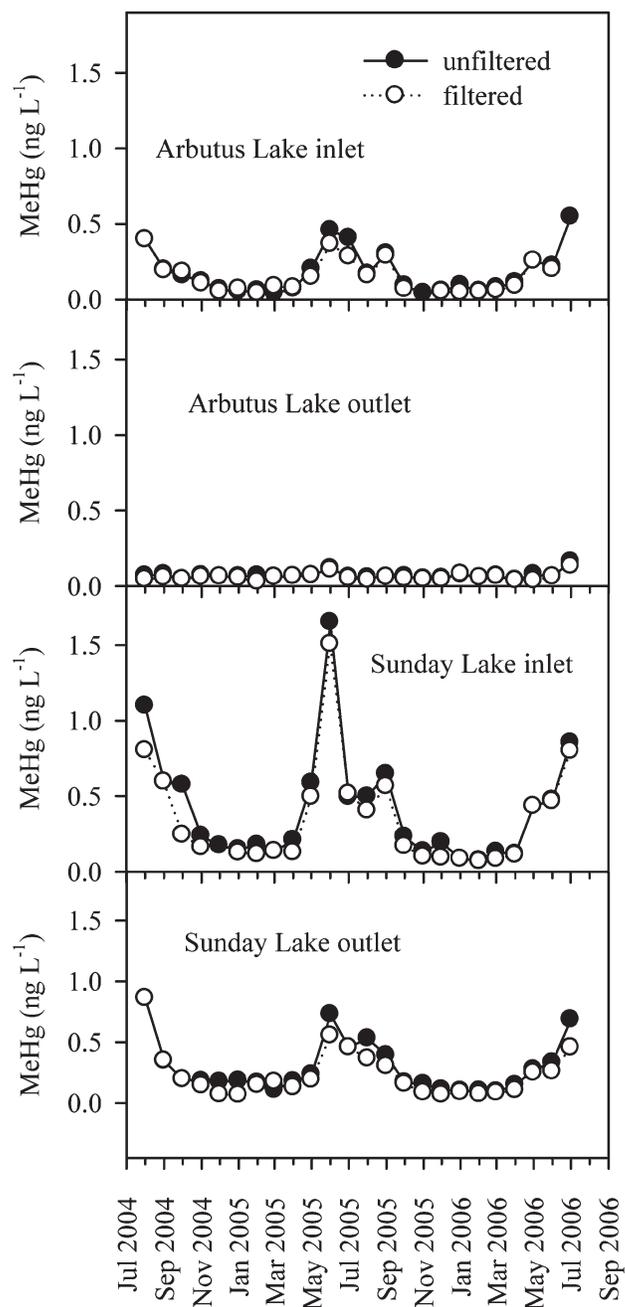

Fig. 2. Temporal patterns in filtered and unfiltered MeHg concentrations (ng L^{-1}) within the inlet and outlet of Arbutus and Sunday Lakes.

Archer Creek supplied 35% of the water input. The remaining 45% of the input was supplied from non-channelized (ungauged) runoff. At the SLW, runoff from the primary inlet (inlet 2) was the predominant source of water to the lake (88%). Runoff from secondary inlet supplied 8% of water to the lake. Non-channelized runoff accounted for 7% and precipitation supplied 1% of the water input to the lake.
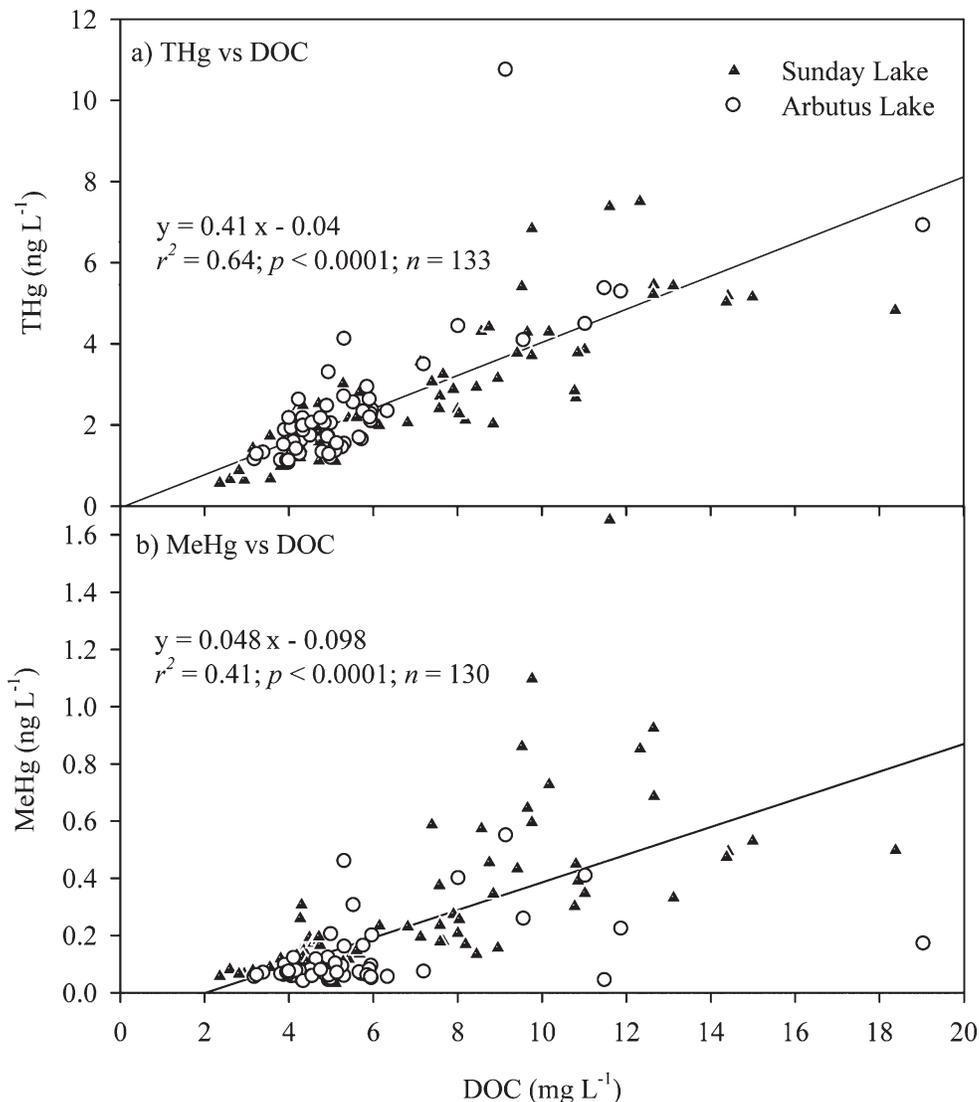
Fig. 3.   Concentrations of (a) THg (ng L^{-1}) and (b) MeHg (ng L^{-1}) as a function of DOC (mg L^{-1}) within surface waters at Arbutus and Sunday Lakes including inlet, outlet, and lake surface. The relationships are significant at $\alpha = 0.05$.

Hg fluxes were estimated for the 2-yr duration of the study (Table 3). Annual Hg fluxes and mass reported herein represent the average of the 2 yr unless mentioned otherwise. Direct wet deposition was a substantial THg flux (6.8 μg m^{-2} yr^{-1} on a lake surface area basis) to Arbutus Lake, with a mass input of 3.3 g yr^{-1} (Table 3). The estimated annual total dry deposition of THg to Arbutus Lake was 1.8 μg m^{-2} yr^{-1}. The total direct deposition flux (wet + dry) and mass input of THg were 8.6 μg m^{-2} yr^{-1} and 4.1 g yr^{-1}, respectively. THg supplied via Archer Creek runoff was 3.3 g yr^{-1} at a rate of 2.5 μg m^{-2} yr^{-1}. A somewhat greater mass of THg was supplied from the ungauged areas of the watershed (4.2 g yr^{-1}) at a flux of 3.1 μg m^{-2} yr^{-1}. The total annual input of THg to the lake was 12.4 g yr^{-1}. Hydrologic loss of THg measured at Arbutus Lake outlet was 4.4 g yr^{-1} at an areal flux of 1.2 μg m^{-2} yr^{-1}. Therefore, 7.3 g yr^{-1} or

an average 64% of the incoming THg was retained in the lake during the study period (Table 3).

At Sunday Lake, the wet deposition flux of THg was slightly elevated (8.1 μg m^{-2} yr^{-1}) compared to Arbutus Lake. Dry deposition amounted to 26% of wet deposition at Arbutus Lake. Applying this ratio, dry deposition at Sunday Lake was estimated to be 2.1 μg m^{-2} yr^{-1}. The total direct deposition flux of THg at Sunday Lake was 10.2 μg m^{-2} yr^{-1}, equivalent to a mass input of 0.6 g yr^{-1}. Most of the terrestrial inputs of THg to Sunday Lake occurred from the primary inlet (inlet 2), which drains 88% of the watershed. The amount of THg supplied annually from inlet 2 was 27.7 g yr^{-1} (92% of incoming THg) at an areal flux of 2.3 μg m^{-2} yr^{-1}. The supply of THg from secondary runoff sources was 1.6 g yr^{-1} at an areal rate of <0.1 μg m^{-2} yr^{-1} (Table 3). The total input of

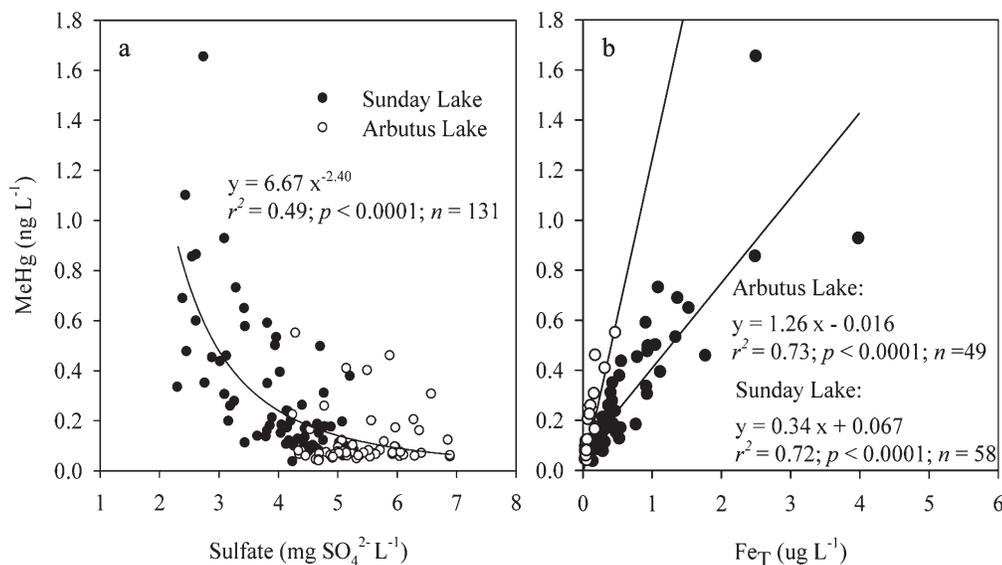Fig. 4. (a) Concentrations of MeHg (ng L^{-1}) as a function of SO$_4^{2-}$ (mg SO$_4^{2-}$ L^{-1}), including inlet, outlet, and lake surface waters at Arbutus Lake and inlet and outlet streams at Sunday Lake. The nonlinear inverse relationship between MeHg and SO$_4^{2-}$ was significant at $\alpha = 0.05$. (b) Concentrations of MeHg (ng L^{-1}) as a function of total dissolved iron (Fe$_T$ in mg L^{-1}). Data include inlet, outlet, and lake surface waters at Arbutus Lake and inlet and outlet streams at Sunday Lake. At both lakes the linear Fe$_T$–MeHg relationship was significant at $\alpha = 0.05$.

THg to Sunday Lake was 30.1 g yr^{-1}. Export of THg at the lake outlet was 30.5 g yr^{-1} with an areal flux of 2.3 μg m^{-2} yr^{-1}. Export of THg from Sunday Lake was slightly greater compared to input, and in contrast to Arbutus Lake no net retention of THg was observed at Sunday Lake. Note that the areal flux of THg from Sunday Lake was considerably greater than that from Arbutus Lake.

Measurements during August 1999–July 2000 indicate that wet deposition of MeHg amounted to 0.55% of the THg wet deposition at ALW (Lindeman 1996). We applied the same ratio for this study to estimate wet MeHg deposition to Arbutus and Sunday Lakes. Direct wet deposition flux of MeHg to the Arbutus Lake surface was 0.04 μg m^{-2} yr^{-1}, supplying a mass input of 0.02 g yr^{-1} MeHg to the lake. Runoff, Archer Creek and ungauged areas together, supplied a total of 0.33 g yr^{-1} of MeHg to Arbutus Lake (Table 3). The areal fluxes of MeHg via Archer Creek and ungauged areas were 0.11 and 0.13 μg m^{-2} yr^{-1} respectively. MeHg export via the outlet was 0.14 g yr^{-1} with an areal flux value (0.04 μg m^{-2} yr^{-1}), equivalent to the wet deposition. Annually, a total of 0.14 g yr^{-1} or 59% of the incoming MeHg was retained within Arbutus Lake.

Direct wet deposition input of MeHg to Sunday Lake (0.003 g yr^{-1}) was an order of magnitude lower compared to Arbutus Lake. Watershed runoff via the primary inlet supplied 95% of the MeHg inputs to the lake (2.97 g yr^{-1}) at an areal flux of 0.25 μg m^{-2} yr^{-1}. Secondary runoff sources supplied a total of 0.17 g yr^{-1} MeHg. The total MeHg input to Sunday Lake was 3.14 g yr^{-1}. Export of MeHg measured at the lake outlet was 2.49 g yr^{-1} at an areal flux value of 0.19 μg m^{-2} yr^{-1}. The total retention of MeHg at Sunday Lake was 0.65 g yr^{-1} or 21% of the incoming MeHg. Note that for both Arbutus and Sunday

Lakes, mass balance calculations suggest that the lakes are net sinks of MeHg. Note that hydrologic Hg budgets were estimated as a function of continuous discharge and monthly Hg concentrations. Hg transport during high-flow events was not the focus of this study. Therefore, the tributary Hg loads reported herein may be slightly underestimated. An analysis of the response of Hg species to hydrologic events of Archer Creek is available in Bushey et al. (2008).

DOC plays a critical role in the transport of Hg species at Arbutus and Sunday Lakes, as evident from the strong DOC–Hg relationships (Fig. 3a,b). At both Arbutus and Sunday Lakes, year-to-year variability in DOC budgets was reflected in Hg budgets (Table 3). In comparison to the first year of study, the second year exhibited relatively greater outflow and less retention of DOC, and correspondingly less retention of THg and MeHg occurred in both lakes (Table 3).

DGM measurements at Arbutus Lake—The average DGM concentration during the summer observations (61.4 $\pm$ 13.9 pg L^{-1}; water temperature 22°C; wind speed 1–6 m s^{-1}; solar radiation mean, 307 W m^{-2}, maximum, 1060 W m^{-2}) was threefold greater compared to DGM concentrations during the fall (19.0 $\pm$ 6.6 pg L^{-1}; water temperature 17°C; wind speed 1–6 m s^{-1}; solar radiation mean, 221 W m^{-2}; solar radiation maximum, 934 W m^{-2}). Photoreduction of Hg^{2+}, caused by solar radiation, has been identified as the primary mechanism in the production of DGM in lake waters (Amyot et al. 1994; O'Driscoll et al. 2003a). Other studies have reported elevated DGM during summer in northern lakes (31–80 pg L^{-1}, Amyot et al. 1997; 76 pg L^{-1}, O'Driscoll et al. 2003a). Modest differences were observed in average specific conductivity (Sp.

Table 3. Watershed drainage areas, annual water budget, fluxes, and mass budgets of THg, MeHg, and DOC at Arbutus and Sunday Lakes during the period August 2004–July 2006. Y1 and Y2 correspond to the budget years August 2004–July 2005 and August 2005–July 2006, respectively. Ŷ represents the average value of Y1 and Y2. Areal fluxes ($\mu g\ m^{-2}\ yr^{-1}$) were presented on the basis of per square meter of watershed drainage area. Percentage retention was estimated by applying Eq. 2 and multiplying the value by 100. NA, not available.

	Area (km²)	Volume (10³ m³)		THg (μg m⁻² yr⁻¹)			MeHg (μg m⁻² yr⁻¹)			DOC (g m⁻² yr⁻¹)			THg (g yr⁻¹)			MeHg (g yr⁻¹)			DOC (10⁶ g yr⁻¹)		
		Y1	Y2	Y1	Y2	Ŷ	Y1	Y2	Ŷ	Y1	Y2	Ŷ	Y1	Y2	Ŷ	Y1	Y2	Ŷ	Y1	Y2	Ŷ
Arbutus Lake																					
Wet deposition*	0.48	544	664	6.9	6.7	6.8	0.04	0.04	0.04	NA	NA	NA	3.3	3.3	3.3	0.02	0.02	0.02	NA	NA	NA
Dry deposition*				1.8	1.8	1.8	NA	NA	NA	NA	NA	NA	0.9	0.9	0.86	NA	NA	NA	NA	NA	NA
Archer creek runoff*	1.35	912	1152	1.8	3.1	2.5	0.09	0.12	0.11	3.8	6.3	5.0	2.4	4.2	3.3	0.13	0.13	0.13	51.7	84.6	68.1
Non-channelized runoff*	1.69	1152	1455	2.3	3.9	3.1	0.12	0.15	0.13	4.8	7.9	6.4	3.0	5.3	4.2	0.16	0.16	0.16	65.3	106.9	86.1
†Outlet	3.52	1716	2701	0.8	1.6	1.2	0.03	0.05	0.04	2.3	4.1	3.2	2.9	5.8	4.4	0.12	0.16	0.14	82.3	145.1	113.7
ΣInput−output‡		892	571	11.9	13.9	12.9	0.2	0.3	0.2	6.3	10.1	8.2	6.7	7.9	7.3	0.19	0.14	0.16	34.7	46.4	40.5
% retention													69.5	57.6	64	61.1	56.8	59.0	29.6	24.2	26.3
Sunday Lake																					
*Wet deposition	0.077	87	94	8.1	8.1	8.1	0.04	0.04	0.04	NA	NA	NA	0.6	0.6	0.6	0.003	0.003	0.003	NA	NA	NA
*Dry deposition				2.11	2.11	2.11	NA	NA	NA	NA	NA	NA	0.16	0.16	0.16	NA	NA	NA	NA	NA	NA
*Inlet 1—secondary	0.90	684	777	0.06	0.08	0.07	0.01	0.01	0.01	0.2	0.3	0.2	0.8	1.1	1.0	0.08	0.12	0.10	2.9	3.7	3.3
*Inlet 2—primary	11.83	8961	10,170	2.4	2.3	2.3	0.30	0.20	0.25	5.6	6.4	6.0	28.4	27.0	27.7	3.60	2.34	2.97	65.8	75.2	70.5
*Non-channelized runoff	0.60	450	510	0.04	0.04	0.04	0.004	0.006	0.005	0.1	0.1	0.1	0.5	0.7	0.6	0.05	0.08	0.07	1.9	2.4	2.2
†Outlet	13.40	10,639	10,842	2.3	2.2	2.3	0.21	0.16	0.19	5.6	6.1	5.8	31.3	29.7	30.5	2.88	2.11	2.49	74.4	82.1	78.3
ΣInput−output		−457	709	10.4	10.4	10.4	0.14	0.10	0.12	0.4	0.6	0.5	−0.8	0.0	−0.4	0.86	0.43	0.65	−3.9	−0.8	−2.4
% retention													−2.5	−0.2	−1.3	23.01	17.02	20.58	−5.6	−1.0	−3.1

THg, total mercury; MeHg, methyl mercury; DOC, dissolved organic carbon;
* Input.
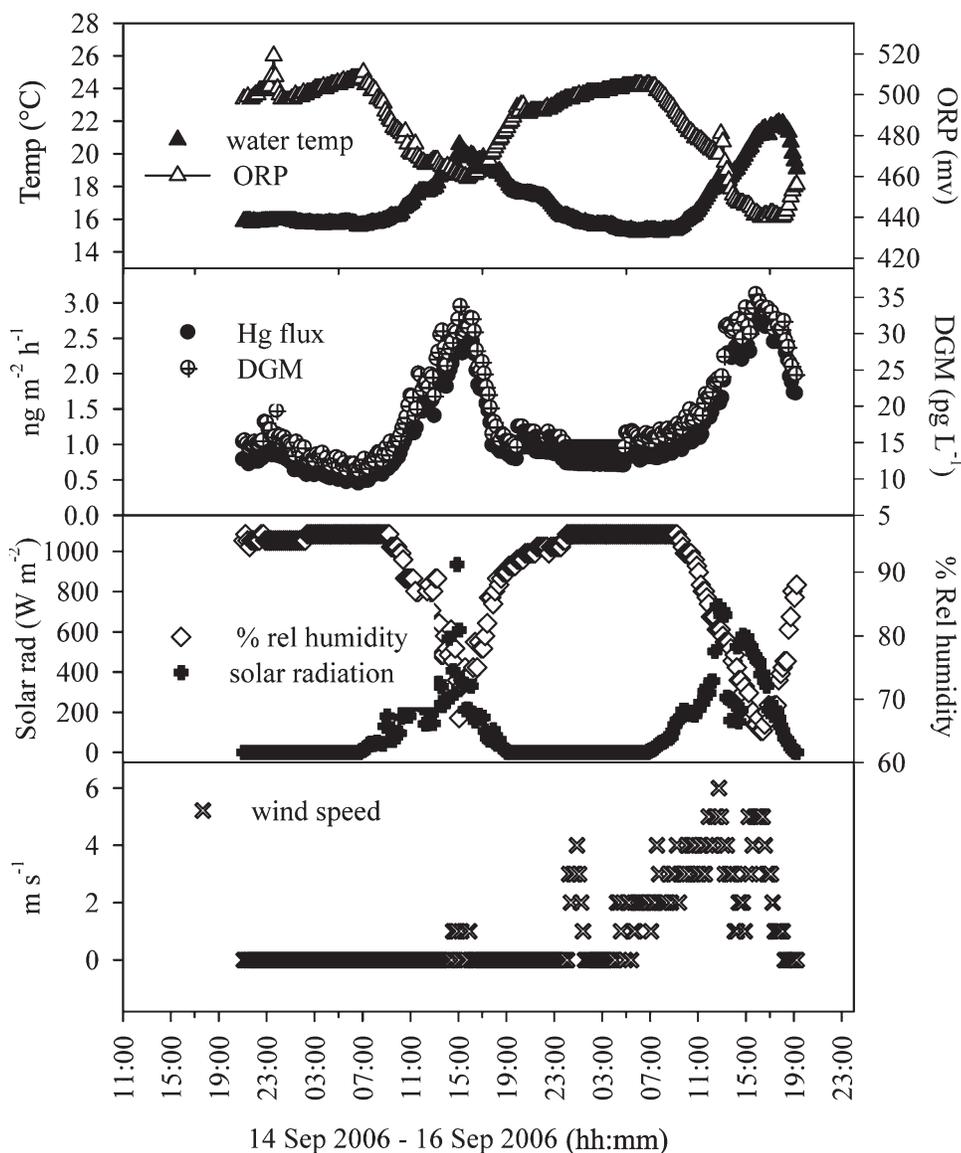† Output.
‡ ΣInput, sum of inputs.

Fig. 5. Diurnal variations in water temperature (°C), oxidation reduction potential (mV), dissolved gaseous Hg (pg L^{-1}), Hg^o flux (ng m^{-2} h^{-1}), percentage relative humidity, solar radiation (W m^{-2}), and wind speed (m s^{-1}) measured at Arbutus Lake during September 14–16, 2006.

Cond.) and DO concentrations during the summer (Sp. Cond. = 21.5 μS cm^{-1}; DO = 7.63 mg L^{-1}) and fall events (Sp. Cond. = 23.5 μS cm^{-1}; DO = 8.92 mg L^{-1}). Microbial reduction of Hg^{2+} to Hg^o has also been suggested (Siciliano et al. 2002). We observed lower oxidation reduction potential (ORP) and more reducing conditions at Arbutus Lake during the summer (379 mV) compared to the fall (482 mV). In addition to higher intensity of solar radiation and water temperature, greater reducing conditions may have facilitated elevated DGM concentrations during summer.

Results of detailed DGM measurements during the fall sampling, including ancillary chemical and meteorological data, are shown in Fig. 5. A mass transfer Hg flux model (Liss and Slater 1974) was applied to estimate Hg^o fluxes.

According to the Hg flux model,

$$F = \frac{C_a - HC_w}{\frac{1}{K_a} + \frac{H}{K_w}} \qquad (4)$$

where F = flux of Hg^o from water to air (ng m^{-2} yr^{-1}), C_a = concentration of Hg^o in air (ng m^{-3}), C_w = concentration of DGM in water (ng m^{-3}), K_a = air mass transfer coefficient of Hg^o (9 m h^{-1}), K_w = water mass transfer coefficient of Hg^o (0.09 m h^{-1}), and H = dimensionless Henry's Law constant. A variable H model developed by Sanemasa (1975) was used:

$$H = 0.0074T + 0.1551 \qquad (5)$$

where H = variable Henry's law constant and T = water

temperature in °C. Schroeder et al. (1992) estimated mass transfer coefficients for Hg° (Ka and Kw) relative to carbon dioxide. A constant air Hg° concentration of 1.5 ng m^{-3} was assumed for the flux calculations (H.-D. Choi pers. comm.).

On average, the Arbutus Lake surface was highly oversaturated with DGM concentrations (mean 19 ng m^{-3}) with respect to ambient Hg° concentrations (1.5 ng m^{-3}). Therefore, a net exchange of Hg° from the water to the atmosphere occurred. The modeled flux followed a strong diurnal pattern that matched the pattern of DGM concentrations at Arbutus Lake. DGM concentrations and Hg° flux remained low during the nighttime. At the start of daylight, DGM concentrations and Hg° flux increased, with peak values occurring past midday (Fig. 5). The mean DGM concentrations during the daytime and nighttime were 22.8 ± 1.5 ng m^{-3} and 14.5 ± 7.0 ng m^{-3}, respectively. The average water to air Hg° flux estimated from the Hg flux model was 1.2 ± 0.7 ng m^{-2} h^{-1}. The average daytime flux (1.6 ± 0.7 ng m^{-2} h^{-1}) was twofold greater than the nighttime flux values (0.7 ± 0.1 ng m^{-2} h^{-1}). Similar differences between daytime (2.1 ± 1.3 ng m^{-2} h^{-1}) and nighttime (0.4 ± 0.4 ng m^{-2} h^{-1}) fluxes were reported for Big Dam West Lake in Canada (O'Driscoll et al. 2003a). DGM concentrations and Hg° flux at Arbutus Lake followed typical diurnal variations in solar radiation and water temperature, and inverse diurnal variations in ORP and percentage relative humidity (Fig. 5).

Discussion

Concentrations of THg at Arbutus (1.1–4.7 ng L^{-1}) and Sunday Lakes (0.3–7.5 ng L^{-1}) were comparable to the range of values reported for other Adirondack lakes (0.8–5.3 ng L^{-1}; Driscoll et al. 1994) and other remote lakes (0.2–15.0 ng L^{-1}; Monson and Brezonik 1998; Dennis et al. 2005). Concentrations of MeHg at Arbutus (0.04–0.46 ng L^{-1}) and Sunday Lakes (0.03–1.65 ng L^{-1}) were also similar to the values reported for other freshwater lakes (0.04–2.20 ng L^{-1}, Watras et al. 1995b; 0.03–0.70 ng L^{-1}, Driscoll et al. 1995; 0.01–3.12 ng L^{-1}, Dennis et al. 2005). The fraction of Hg present as MeHg (% MeHg) was substantially greater at the inlets of Sunday Lake ($10.4 \pm 4.8\%$) compared to Arbutus Lake ($4.7 \pm 3.3\%$). Concentrations of MeHg in catchment runoff are often reported as a function of percentage wetlands within the watershed (Driscoll et al. 1995; Watras et al. 1995; Shanley et al. 2005). Many Adirondack lakes have a high percentage of MeHg (approx. 10%; Driscoll et al. 1995) due the abundance of wetlands in the region.

Annual evasion rates—O'Driscoll et al. (2003a) found that a time shifted solar-radiation model was a good predictor of diurnal Hg° flux compared to previously published evasion models. A significant correlation was observed between Hg° flux and solar radiation at Arbutus Lake ($r = 0.52$) for measurements made during September 2006. However, using cross-correlation analysis a substantial improvement in correlation was observed for a 90° shift in solar radiation ($r = 0.75$, $p < 0.0000$; Eq. 6).

$$\text{Hg° flux} = 2.81 \text{ solar radiation}_{(90 \text{ min prior})} + 0.96 \quad (6)$$

where Hg° flux and solar radiation are expressed in ng m^{-2} h^{-1} and kw m^{-2}, respectively.

Peaks and minima in solar radiation occurred 90 min prior to corresponding peaks in Hg° flux at Arbutus Lake. O'Driscoll et al. (2003a) reported a similar range of time delay associated with solar radiation–Hg° flux for Canadian lakes (65–90 min). These observations indicate that in northern lakes the production of Hg° and subsequent exchange to the overlying atmosphere is delayed approximately 65–90 min following the peak in solar radiation. Differences in time lag and rates of DGM production between different lakes may be controlled primarily by DOC content and structure. Amyot et al. (1997) compared lakes with low and high DOC, and found DGM production was several-fold greater in low DOC lakes. In another study, for a similar range in DOC concentration DGM production was lower in lakes with clear-cut watershed compared to reference lakes, and DOC structure was found to be an important factor controlling this response (O'Driscoll et al. 2004).

The solar radiation model was applied to estimate annual Hg° loss from Arbutus Lake. Nighttime fluxes were assumed constant throughout the open water period (mean, 0.7 ± 0.14 ng m^{-2} h^{-1}). Daytime fluxes were estimated by applying solar radiation observed at the HWF using the data from the Clean Air Trends Network. Daytime flux measured on-site during September 2006 (1.6 ± 0.7 ng m^{-2} h^{-1}) was equivalent to the value estimated by the model for the same period (1.6 ± 0.6 ng m^{-2} h^{-1}). Assuming that Hg° loss is zero for the ice-cover period at Arbutus Lake (December–March), annual evasion losses of 7.80 and 7.73 μg m^{-2} yr^{-1} were estimated for year 1 and year 2 of the study period, respectively. The net loss of Hg° at Arbutus Lake was therefore slightly greater than the areal evasion fluxes estimated for the forested upland at the HWF (6.3 μg m^{-2} yr^{-1}; Choi and Holsen pers. comm.), likely because of the attenuation of solar radiation by forest canopy. Annual evasion rates estimated at Arbutus Lake were comparable to the upper end of the values reported for Wisconsin lakes (0.72 to 5.2 μg m^{-2} yr^{-1}; Watras et al. 1994). Note, however, that the mass supply of THg we observed at Arbutus Lake is considerably greater than the values reported for the Wisconsin seepage lakes.

Hg volatilization is highly variable spatially and seasonally, and therefore there is considerable uncertainty associated with our annual volatilization rates. The production of DGM is dependent upon dissolved THg concentrations (Gao et al. 2006). For large lakes with highly variable tributary input Hg loads, the uncertainties in annual Hg volatilization rates are large (Gao et al. 2006). At Arbutus Lake, annual Hg loading is less variable (Table 3), and direct estimates of DGM improved our estimate of Hg volatilization rates. Nevertheless, additional detailed measurements are needed to better quantify and characterize this important loss mechanism in lakes.

Hg mass balances—Wet deposition fluxes of THg at Sunday Lake (8.1 μg m^{-2} yr^{-1}) and Arbutus Lake (6.1 μg m^{-2} yr^{-1}) are within the current rates reported for the northeastern U.S. (3.8–12.6 μg m^{-2} yr^{-1}; Driscoll et al. 2007) and northern remote temperate forest (5–15 μg m^{-2} yr^{-1}; Grigal 2002). Terrestrial runoff fluxes (0.04–2.4 μg m^{-2} yr^{-1}) were small relative to atmospheric fluxes (8.6–11.2 μg m^{-2} yr^{-1}; wet + dry Hg deposition) and therefore Sunday and Arbutus watersheds were large sinks of atmospheric Hg deposition.

The estimated annual net removal of THg at Arbutus Lake (7.3 g yr^{-1}; Table 3) was likely from loss caused by sedimentation and Hg^o volatilization. Our estimate of annual evasion rate (7.8 μg m^{-2} yr^{-1}) indicates that 3.7 g yr^{-1} of Hg was lost through volatilization. The estimated rate of Hg loss via volatilization was approximately equivalent to that of the direct atmospheric deposition flux (8.6 μg m^{-2} yr^{-1}) to the Arbutus Lake surface.

Annual sedimentation loss of THg at Arbutus Lake, estimated as the discrepancy in the mass balance, was 3.5 g yr^{-1} at an areal rate of 7.3 μg m^{-2} yr^{-1}. Therefore, the net removal of 7.3 g yr^{-1} was balanced by Hg loss through volatilization (3.7 g yr^{-1}) and sediment deposition (3.5 g yr^{-1}). Estimated sediment deposition rate of THg at Arbutus Lake was within the range of values previously reported for Adirondack lakes (4.9–64.3 μg m^{-2} yr^{-1}; Lorey and Driscoll 1999), Wisconsin lakes (4.4–9.3 μg m^{-2} yr^{-1}; Watras et al. 1994) and Swedish lakes (7–30 μg m^{-2} yr^{-1}; Meili et al. 1991). Applying a flux ratio of 3.7 reported for Adirondack lakes (Lorey and Driscoll 1999), we estimate a preindustrial sediment deposition rate of 2.0 μg m^{-2} yr^{-1} for Arbutus Lake.

The rates of MeHg inputs from SLW and ALW were of similar magnitude (0.26 and 0.21 μg m^{-2} yr^{-1}, respectively). Note that inputs of MeHg from atmospheric deposition are approximately an order of magnitude lower ($\sim$0.04 μg m^{-2} yr^{-1}). Terrestrial transformations, particularly methylation in wetlands and transport in runoff, constitute the predominant mechanism by which MeHg is supplied to downstream drainage lakes (Harris et al. 2007). Net retention and loss of MeHg occurred at Sunday and Arbutus Lakes, as inferred from lower export compared to total input (Table 3). In contrast to THg, which exhibited relatively conservative transport, in-lake processes influenced MeHg loss at Sunday Lake. The estimated rates of net MeHg loss (based on lake surface area) were 8.39 μg m^{-2} yr^{-1} at Sunday Lake and 0.45 μg m^{-2} yr^{-1} at Arbutus Lake.

Greater net loss of MeHg occurred during the growing season compared to the nongrowing season. At both Arbutus and Sunday Lakes, the areal fluxes of input MeHg during the growing season were 0.15 μg m^{-2} period^{-1}, compared to 0.09 μg m^{-2} period^{-1} during the nongrowing season. A net retention of 90% of the incoming MeHg occurred during the growing season compared to 72% during the nongrowing season at Arbutus Lake. A similar pattern was observed at Sunday Lake, where 36% of the incoming MeHg was retained during the growing season compared to 26% during the nongrowing season.

Annual budget estimates indicate that approximately 20% and 60% of the incoming MeHg was retained at Sunday and Arbutus Lake, respectively. High rates of net loss suggest that MeHg undergoes complex in-lake processing, including bioaccumulation in the aquatic food web, demethylation, and/or loss through sedimentation (Ullrich et al. 2001; Mason and Benoit 2003). There has been increasing evidence that photodegradation could be an important removal mechanism for MeHg in lakes (Sellers et al. 2001).

Several investigators have emphasized the importance of in-lake production relative to external sources of MeHg (Sellers et al. 2001; Shanley et al. 2005; Watras et al. 2005). Watras et al. (2005) suggested that for wetland-dominated lakes with HRT greater than 6 months, in-lake methylation would be a dominant component of the MeHg budget. Direct atmospheric deposition MeHg inputs (up to 0.1 μg m^{-2} yr^{-1}; Watras et al. 1995*a*; Sellers et al. 2001) and net production rates of MeHg reported for northern wetlands (0.2–0.6 μg m^{-2} yr^{-1}; Driscoll et al. 1998; Harris et al. 2007) are substantially lower than values reported for in-lake methylation (0.3–3 μg m^{-2} yr^{-1}; Rudd 1995). Watras et al. (1995) reported an order of magnitude higher rate of in-lake methylation ranging from 18 to 36 μg m^{-2} yr^{-1} for a dimictic seepage lake in Wisconsin. Note that, in contrast to these studies, we observed that Adirondack lakes in the current study are net sinks of MeHg. One possible explanation for this pattern is that the yield of MeHg is much greater for wetland-dominated catchments, and loss process will dominate over within-lake MeHg production.

Factors affecting Hg cycling in lakes—Budget comparisons provide useful insights on major physical and chemical controls on Hg cycling. Mass inputs of THg and MeHg from watershed runoff were an order of magnitude greater at Sunday Lake compared to Arbutus Lake (Table 3). Higher areal Hg loading to Sunday Lake was primarily driven by greater watershed to lake surface area ratio and wetland processes because of a higher percentage of wetland area (174 and 20%, respectively) compared to Arbutus Lake (7.3 and 4%, respectively). The size of the lake relative to the watershed influences the relative contributions of Hg inputs from atmospheric deposition and thus has implications for bioaccumulation. At Arbutus Lake (0.48 km^2), direct atmospheric deposition supplied 36% of annual THg inputs, compared to 2% at Sunday Lake. Atmospheric Hg is associated mostly with water-soluble Cl$^-$, OH$^-$, and SO$_4^{2-}$ complexes and is likely more readily bioavailable for methylation and biotic uptake than lakes that receive inputs largely from drainage water, where Hg is likely less bioavailable because of association with DOC or particulate matter.

We observed major differences in Hg and ancillary chemistry between Arbutus and Sunday Lakes. Concentrations of metals (Fe, Mn, and Al) and DOC were substantially higher and SO$_4^{2-}$ and pH were considerably lower at Sunday Lake compared to Arbutus Lake (Table 2). In particular, DOC and pH have complex and poorly understood roles in Hg dynamics. Organic solutes appear to be closely associated
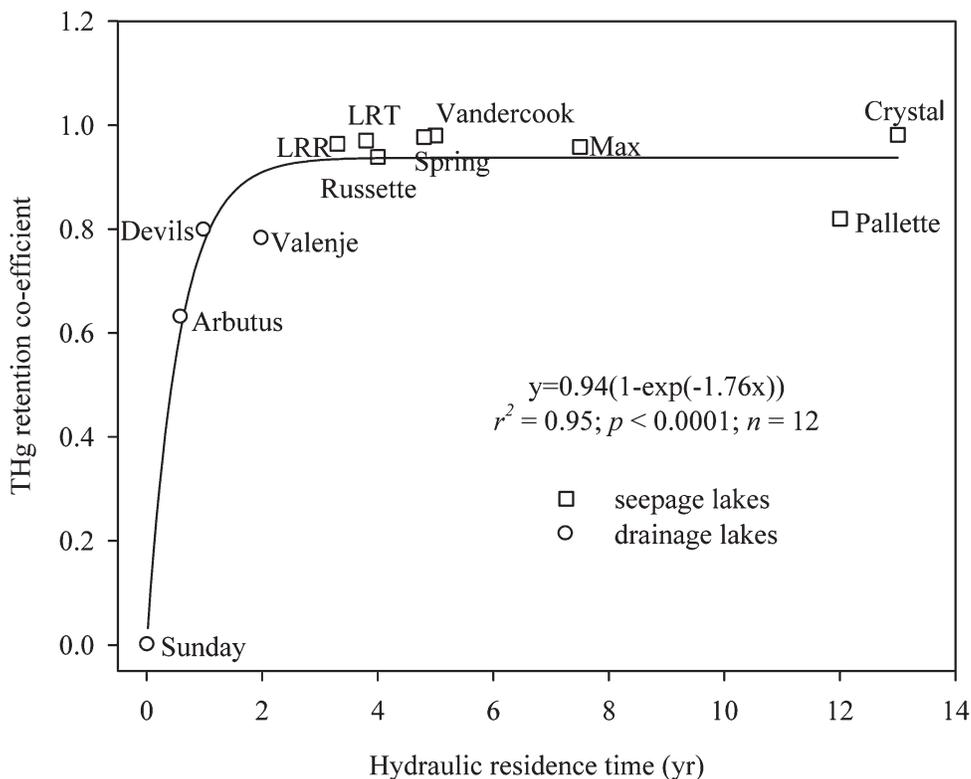
Fig. 6. Retention coefficient (*R*) of THg as a function of hydraulic residence time of water (yr) from various lakes. In addition to the current study, data were obtained from Watras et al. (1994); Kotnik et al. (2002); and Hines and Brezonik (2007) (*see* Table 4).

with THg and MeHg transport to lakes (Dennis et al. 2005). However, as organic ligands, these solutes may also reduce bioavailability (Hudson et al. 1994). Inputs of other metals (e.g., Al, Fe) may influence bioavailability (Driscoll et al. 1994) and methylation (Ullrich et al. 2001). DOC also is a critical controller of the attenuation of solar radiation (Effler et al. 1985) and therefore likely influences photoreduction and photodegradation of MeHg.

HRT is among the most important physical factors that influence Hg budgets in lakes (Sellers et al. 2001; Watras et al. 2005). A cross-site analysis that includes data from drainage and seepage lakes in the literature reveals that in-lake removal of THg increases with increasing HRT (Fig. 6). Because of negligible THg removal at Sunday Lake, the THg retention value was set to zero (actual value $= -1.3$) for the purpose of this analysis. It appears that for

Table 4. Estimates of THg retention coefficients (R_{THg}) and mass transfer coefficients (S_{THg}) for lakes with various hydraulic residence time and mean depth. Retention coefficients (R_{THg}) were estimated from mass balance data using Eq. 2. Mass transfer coefficients (S_{THg}) were estimated from Eq. 3.

Lake	Type	Z (m)	HRT (yr)	R_{THg}	S_{THg} (m yr^{-1})	Reference
Little Rock—treatment, Wisconsin	Seepage	3.9	3.8	0.97	33.53	Watras et al. 1994
Little Rock—reference, Wisconsin	Seepage	3.1	3.3	0.96	25.05	Watras et al. 1994
Vandercook Lake, Wisconsin	Seepage	4.7	5	0.98	45.96	Watras et al. 1994
Pallette Lake, Wisconsin	Seepage	9.6	12	0.82	3.64	Watras et al. 1994
Max Lake, Wisconsin	Seepage	2.9	7.5	0.96	8.80	Watras et al. 1994
Crystal Lake, Wisconsin	Seepage	10.4	13	0.98	41.60	Watras et al. 1994
Russette Lake, Wisconsin	Seepage	3.9	4	0.94	14.95	Watras et al. 1994
Devils Lake, Wisconsin	Drainage	3	1	0.80	11.81	Watras et al. 2005
Lake Velenje, Slovenia	Drainage	17.9	2	0.78	31.96	Kotnik et al. 2002
Spring Lake, Minnesota	Seepage	2	4.8	0.98	17.74	Hines and Breznoik 2007
Arbutus Lake, New York	Drainage	3	0.6	0.64	9.09	Current study
Sunday Lake, New York	Drainage	2.5	0.02	0.00	0.00	Current study

Mean = 20.3±15.0 m yr^{-1}. THg, total mercury.

drainage lakes, typically characterized by HRT values less than 3 yr, the variation in HRT is critical in determining net THg retention. For lakes with HRT >4 yr (i.e., seepage lakes), a nearly complete removal of THg was observed. Similar patterns have been observed for SO_4^{2-}, NO_3^-, and phosphorus removal in lakes (Reckhow and Chapra 1983; Kelly et al. 1987).

Using Eq. 3, the estimated average S_{THg} for the lakes was 20.3 ± 15 m yr^{-1} (Table 4). Note the variation in the estimated S_{THg} was large ($\pm 74\%$) in comparison to the narrow range of values estimated for SO_4^{2-} and NO_3^- by Kelly et al. (1987). This variation in S_{THg} among lakes suggests that in-lake removal of THg is not entirely limited by the inflow and size of the lake, and likely involves several other unaccounted controlling factors, including binding with DOC or particulate matter, pH effects, and the distribution of retention mechanism between evasion and sedimentation.

Hg budgets and the controlling physical and chemical characteristics were evaluated for two different remote lakes in the Adirondack region of New York. Landscape factors such as the ratio of watershed to lake area, percentage of the watershed occurring as wetlands, and size of the lake are important controllers of both THg and MeHg inputs and retention in the lakes. HRT largely determines the extent of within-lake processing and retention of THg. SLW was fourfold larger with greater percentage wetland coverage than ALW, and correspondingly terrestrial input of THg at Sunday Lake was an order of magnitude greater compared to Arbutus Lake. However, most of the annual THg input was exported at Sunday Lake as a result of a very short HRT. Such relatively conservative transport of THg has not been reported for other lakes. With increases in HRT, THg undergoes complex within-lake cycling. At Arbutus Lake the HRT is 0.6 yr, and lake mass balance suggests that 64% of the incoming THg was removed through sedimentation and volatilization. Estimates of Hg° volatilization rates at Arbutus Lake indicate that most of the Hg directly deposited to the lake surface was reemitted and was of the same magnitude as THg sedimentation. A cross-site analysis of THg mass transfer coefficients reveals that in addition to HRT and mean depth, other factors likely are important for within-lake removal processes. In contrast to other studies in the literature, mass balances indicate that Sunday and Arbutus Lakes were net sinks for MeHg inputs. In comparison to THg, within-lake cycling of MeHg was less influenced by HRT. We hypothesize that in-lake MeHg cycling will be important even for lakes that are characterized by short HRT (e.g., Sunday Lake).

About 21% of total atmospheric THg deposition to lake surface in the Adirondacks was in the form of dry deposition, compared to 24% reported for Wisconsin lakes (Lamborg et al. 1995). Adirondack lakes with lower watershed to lake surface area ratio such as Arbutus (7.3:1) are susceptible to labile atmospheric Hg inputs, which likely is important in the supply of bioavailable Hg. At Sunday Lake, elevated concentrations of metals including Mn, Fe, and Al might compete for DOC binding, thus increasing Hg bioavailability.

References

ABABNEH, F. A., S. L. SCOTT, H. A. AL-REASI, AND D. R. S. LEAN. 2006. Photochemical reduction and reoxidation of aqueous mercuric chloride in the presence of ferrioxalate and air. Sci. Total Environ. **367:** 831–839.

AMYOT, M., G. MIERLE, D. R. S. LEAN, AND D. J. MCQUEEN. 1994. Sunlight-induced formation of dissolved gaseous mercury in lake waters. Environ. Sci. Technol. **28:** 2366–2371.

———, ———, ———, AND ———. 1997. Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes. Geochim. Cosmochim. Acta **61:** 975–987.

AMERICAN PUBLIC HEALTH ASSOCIATION, AMERICAN WATER WORKS ASSOCIATION, AND WATER ENVIRONMENT FEDERATION. 1998. Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association, American Water Works Association, and Water Environment Federation.

BLOOM, N. S., AND OTHERS. 1999. Speciation and cycling of mercury in Lavaca Bay, Texas, sediments. Environ. Sci. Technol. **33:** 663–669.

BUSHEY, J. T., C. T. DRISCOLL, M. J. MITCHELL, P. SELVENDIRAN, AND M. R. MONTESDEOCA. 2008. Mercury transport in response to storm events from a northern forest landscape. Hydrol. Process. **22:** 4813–4826, doi:10.1002/hyp.7091.

DENNIS, I. F., AND OTHERS. 2005. Distribution patterns of mercury in lakes and rivers of northeastern North America. Ecotoxicology **14:** 113–123.

DOMMERGUE, A., C. FERRARI, L. POISSANT, A. GAUCHARD, AND C. BOUTRON. 2003. Diurnal cycles of gaseous mercury within the snowpack at Kuujjuarapik/Whapmagoostui, Québec, Canada. Environ. Sci. Technol. **37:** 3289–3297.

DRISCOLL, C. T., V. BLETTE, C. YAN, C. L. SCHOFIELD, R. MUNSON, AND J. HOLSAPPLE. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. Water Air Soil Pollut. **80:** 499–508.

———, J. HOLSAPPLE, C. L. SCHOFIELD, AND R. MUNSON. 1998. The chemistry and transport of mercury in a small wetland in the Adirondack region of New York, USA. Biogeochemistry **40:** 137–146.

———, C. YAN, C. L. SCHOFIELD, R. MUNSON, AND J. HOLSAPPLE. 1994. The mercury cycle and fish in the Adirondack lakes. Environ. Sci. Technol. **28:** 136–143.

———, AND OTHERS. 2007. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. Bioscience **57:** 17–28.

EFFLER, S. W., G. C. SCHAFRAN, AND C. T. DRISCOLL. 1985. Partitioning light attenuation in an acidic lake. Can. J. Fish. Aquat. Sci. **42:** 1707–1711.

ENVIRONMENTAL PROTECTION AGENCY. 1996. Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303).

———. 2001. Method 1630: Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS (EPA-821-R-01-020, January 2001). U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303).

———. 2002. Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (EPA-821-R-01-019, August 2002). U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303).

EVERS, D. C., AND OTHERS. 2007. Identification and evaluation of biological hotspots of mercury in the northeastern U.S. and eastern Canada. Bioscience **57:** 29–43.

FITZGERALD, W., D. ENGSTROM, R. MASON, AND E. NATER. 1998. The case for atmospheric mercury contamination in remote areas. Environ. Sci. Technol. **32:** 1–7.

GAO, N., AND OTHERS. 2006. Mass balance assessment for mercury in Lake Champlain. Environ. Sci. Technol. **40:** 82–89.

GRIGAL, D. F. 2002. Inputs and outputs of mercury from terrestrial watersheds: A review. Environ. Rev. **10:** 1–39.

HARRIS, R. C., AND OTHERS. 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. Proc. Natl. Acad. Sci. USA **104:** 16586–16591.

HINES, N. A., AND P. L. BREZONIK. 2007. Mercury inputs and outputs at a small lake in northern Minnesota. Biogeochemistry **84:** 265–284.

HUDSON, R. J. M., S. A. GHERINI, C. J. WATRAS, AND D. B. PORCELLA. 1994. Modeling the biogeochemical cycle of mercury in lakes: The mercury cycling model and its application to the MTL study lakes, p. 473–523. *In* C. J. Watras and J. W. Huckabee [eds.], Mercury pollution integration and synthesis. Lewis.

JEREMIASON, J., AND OTHERS. 2006. Sulfate addition increases methylmercury production in an experimental wetland. Environ. Sci. Technol. **40:** 3800–3806.

KAMMAN, N. C., AND OTHERS. 2005. Mercury in freshwater fish of northeast North America—a geographic perspective based on fish tissue monitoring perspective based on fish tissue monitoring databases. Ecotoxicology **14:** 163–180.

KELLY, C. A., AND OTHERS. 1987. Prediction of biological acid neutralization in acid-sensitive lakes. Biogeochemistry **3:** 129–141.

KOTNIK, J., M. HOVART, V. FAJON, AND M. LOGAR. 2002. Mercury in small freshwater lakes: A case study; Lake Velenje, Slovenia. Water Air Soil Pollut. **134:** 319–339.

LAI, S.-O., AND OTHERS. 2007. Estimation of mercury loadings to Lake Ontario: Results from the Lake Ontario atmospheric deposition study (LOADS). Atmos. Environ. **41:** 8205–8219, doi:10.1016/j.atmosenv.2007.06.035.

LAMBORG, C., W. FITZGERALD, G. VANDAL, AND K. ROLFHUS. 1995. Atmospheric mercury in northern Wisconsin: Sources and species. Water Air Soil Pollut. **80:** 189–198.

LANDIS, M. S., AND G. J. KEELER. 2002. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan Mass Balance Study. Environ. Sci. Technol. **36:** 4518–4524.

LINDEMAN, M. A. 1996. The cycling and fate of mercury in the Sunday Lake Watershed, Adirondack Region of New York. M.S. thesis. Syracuse Univ.

LISS, P. S., AND P. G. SLATER. 1974. Flux of gases across the air–sea interface. Nature **247:** 181–184.

LOREY, P., AND C. T. DRISCOLL. 1999. Historical trends of mercury deposition in Adirondack lakes. Environ. Sci. Technol. **33:** 718–722.

MASON, R. P., AND J. M. BENOIT. 2003. Organomercury compounds in the environment, p. 57–99. *In* P. Graig [ed.], Organometallic compounds in the environment. Wiley.

McHALE, M. R., C. P. CIRMO, M. J. MITCHELL, AND J. J. McDONNELL. 2004. Wetland nitrogen dynamics in an Adirondack forested watershed. Hydrol. Process. **18:** 1853–1870.

MEILI, M., A. IVERFELDT, AND L. HÅKANSON. 1991. Mercury in the surface water of Swedish forest lakes—concentrations, speciation and controlling factors. Water Air Soil Pollut. **56:** 439–453.

MITCHELL, M. J., R. C. SANTORE, C. T. DRISCOLL, AND B. R. DHAMALA. 1998. Forest soil sulfur in the Adirondack Mountains: Response to chemical manipulations. Soil Sci. Soc. Am. J. **62:** 272–280.

MONSON, B. A., AND P. L. BREZONIK. 1998. Seasonal patterns of mercury species in water and plankton from softwater lakes in Northeastern Minnesota. Biogeochemistry **40:** 147–162.

O'DRISCOLL, N. J., S. BEAUCHAMP, S. D. SICILIANO, A. N. RENCZ, AND D. R. S. LEAN. 2003a. Continuous analysis of dissolved gaseous mercury (DGM) and mercury flux in two freshwater lakes in Kejimkujik Park, Nova Scotia: Evaluating mercury flux models with quantitative data. Environ. Sci. Technol. **37:** 2226–2235.

———, D. R. S. LEAN, L. LOSETO, R. CARIGNAN, AND S. D. SICILIANO. 2004. The effect of dissolved organic carbon on the photoproduction of dissolved gaseous mercury in lakes and the potential impacts of forestry. Environ. Sci. Technol. **38:** 2664–2672.

———, S. D. SICILIANO, AND D. R. S. LEAN. 2003b. Continuous analysis of dissolved gaseous mercury in freshwater lakes. Sci. Total Environ. **300:** 285–294.

REA, A. W., S. E. LINDBERG, AND G. J. SCHERBATSKOY. 2001. Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. Atmos. Environ. **35:** 3453–3462.

RECKHOW, K. H., AND S. C. CHAPRA. 1983. Engineering approaches for lake management, V. 1: Data analysis and empirical modeling. Butterworth.

RUDD, J. W. M. 1995. Sources of methyl mercury to freshwater ecosystems: A review. Water Air Soil Pollut. **80:** 697–713.

SANEMASA, I. 1975. The solubility of elemental mercury vapor in water. Bull. Chem. Soc. Japan **48:** 1795–1798.

SCHROEDER, W. H., O. LINDQVIST, J. MUNTHE, AND Z. XIAO. 1992. Volatilization of mercury from lake surfaces. Sci. Total Environ. **125:** 47–66.

SELLERS, P., C. A. KELLY, AND J. M. M. RUDD. 2001. Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources. Limnol. Oceanogr. **46:** 623–631.

SELVENDIRAN, P., C. T. DRISCOLL, J. T. BUSHEY, AND M. R. MONTESDEOCA. 2008. Wetland influence on mercury fate and transport in a temperate forested watershed. Environ. Pollut. **154:** 46–55.

SHANLEY, J. B., N. C. KAMMAN, T. A. CLAIR, AND A. CHALMERS. 2005. Physical controls on total and methylmercury concentrations in streams and lakes of the Northeastern USA. Ecotoxicology **14:** 125–134.

SICILIANO, S. D., N. J. O'DRISCOL, AND D. LEAN. 2002. Microbial reduction and oxidation of mercury in freshwater lakes. Environ. Sci. Technol. **36:** 3064–3068.

TOSSELL, 1998. Theoretical study of the photodecomposition of methyl Hg complexes. J. Phys. Chem. **102:** 3587–3591.

ULLRICH, S. M., T. W. TANTON, AND S. A. ABDRASHITOVS. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. Crit. Rev. Environ. Sci. Technol. **31:** 241–293.

VAN LOON, L., E. MADER, AND S. L. SCOTT. 2000. Reduction of the aqueous mercuric ion by sulfite: UV spectrum of $HgSO_3$ and its intramolecular redox reaction. J. Phys. Chem. **104:** 1621–1626.

WATRAS, C. J., N. S. BLOOM, S. A. CLAAS, K. A. MORRISON, C. C. GILMOUR, AND S. R. CRAIG. 1995a. Methylmercury production in the anoxic hypolimnion of a dimictic seepage lake. Water Air Soil Pollut. **80:** 735–745.

———, K. A. MORRISON, J. S. HOST, AND N. S. BLOOM. 1995b. Concentration of mercury species in relationship to other site-specific factors in the surface waters of northern Wisconsin lakes. Limnol. Oceanogr. **40:** 556–565.

————, AND OTHERS. 1994. Sources and fate of mercury and methylmercury in Wisconsin lakes, p. 153–180. *In* C. J. Watras and J. W. Huckabee [eds.], Mercury pollution: Integration and synthesis. Lewis.

————, AND OTHERS. 2005. Sources of methylmercury to a wetland-dominated lake in Northern Wisconsin. Environ. Sci. Technol. **39:** 4747–4758.

XIAO, Z. F., D. STROMBERG, AND O. LINDQVIST. 1995. Influence of humic substances on photolysis of divalent mercury in aqueous-solution. Water Air Soil Pollut. **80:** 789–798.

ZHANG, H., AND S. E LINDBERG. 2001. Sunlight and iron (III)-induced photochemical production of dissolved gaseous mercury in freshwater. Environ. Sci. Technol. **35:** 928–935.