

Wetland influence on mercury fate and transport in a temperate forested watershed

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*Wetlands are sources of THg and MeHg; the production of MeHg is seasonally dependent
and driven by sulfate reduction in wetlands.*

Abstract

The transport and fate of mercury (Hg) was studied in two forest wetlands; a riparian peatland and an abandoned beaver meadow. The proportion of total mercury (THg) that was methyl mercury (% MeHg) increased from 2% to 6% from the upland inlets to the outlet of the wetlands. During the growing season, MeHg concentrations were approximately three times higher (0.27 ng/L) than values during the non-growing season (0.10 ng/L). Transport of Hg species was facilitated by DOC production as indicated by significant positive relations with THg and MeHg. Elevated concentrations of MeHg and % MeHg (as high as 70%) were found in pore waters of the riparian and beaver meadow wetlands. Groundwater interaction with the stream was limited at the riparian peatland due to the low hydraulic conductivity of the peat. The annual fluxes of THg and MeHg at the outlet of the watershed were 2.3 and 0.092 $\mu\text{g}/\text{m}^2\text{-year}$ respectively.

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1. Introduction

High concentrations of mercury (Hg) in water and fish have been found in many lakes in the Adirondack region of New York (Driscoll et al., 1995, 1994; Dennis et al., 2005). Recent studies have identified biological Hg hotspots in the northeastern US and southeastern Canada, including the western Adirondacks, where Hg concentrations in biota are in excess of human and wildlife health criteria (Evers et al., 2007; Driscoll et al., 2007). Human and ecological health concerns are attributed to exposure to methyl mercury (MeHg), due to its tendency to strongly bioaccumulate in the aquatic food chain

(Wiener et al., 2002). Although atmospheric inputs of MeHg are typically low, terrestrial landscapes, especially wetlands, constitute an important source of MeHg to downstream aquatic ecosystems (e.g., Gilmour et al., 1998; St. Louis et al., 1994).

Wetlands play an important role in the concentrations and mobility of Hg (e.g., St. Louis et al., 1996; Branfireun et al., 1998). Various studies have identified wetlands as a sink of total mercury (THg), but often as a net source of MeHg (e.g., Driscoll et al., 1998; Allan and Heyes, 1998; Galloway and Branfireun, 2004; Grigal et al., 2000). Sulfate-reducing bacteria (SRB) mediate the conversion of ionic mercury (Hg^{2+}) to MeHg (Benoit et al., 2003). Uplands are critical Hg sources to the methylation zones in wetlands.

The production of MeHg and transport of Hg species are influenced by several watershed level processes. Methylation of Hg in wetlands is a complex function of various physical (temperature, water saturation) and chemical (nutrient supply, pH, anoxia) conditions, and the activity of microbial

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populations, particularly SRB (Gustin et al., 2006; Benoit et al., 2003). The transport of Hg from wetlands is influenced by hydrology, land cover, soil type, and the character and availability of binding ligands (Branfireun and Roulet, 2002; St. Louis et al., 1994; Hurley et al., 1995; Babiarz et al., 1998). Seasonal changes in watershed saturation conditions, temperature, microbial activity, and discharge influence both production and transport mechanisms of Hg species. Maximum concentrations of MeHg in surface waters are often found during warmer months (Watras et al., 2005; Babiarz et al., 1998; Driscoll et al., 1998), coinciding with warmer temperature, increased microbial activity and low flow conditions. High runoff accounts for a substantial portion of Hg flux from watersheds (Babiarz et al., 1998), with Hg mobility linked to particulate matter (Scherbatskoy et al., 1998; Shanley et al., 2002; Lawson et al., 2001; Allan and Heyes, 1998) and/or dissolved organic carbon (DOC; Mast et al., 2005; Shanley et al., 2002).

St. Louis et al. (1996) compared a valley-bottom, a riverine, and a basin wetland, concluding that all three wetland types are sources of MeHg. However, the magnitude of MeHg production was found to be related to differences in the internal hydrology of the wetlands. Peatlands and near stream riparian zones can be hotspots of MeHg production (e.g., Branfireun et al., 1996; Bishop et al., 1995). The high rates of organic matter decomposition, sulfate-reducing conditions, and the potential for *in situ* methylation underscore these wetlands as important source areas of MeHg (Moore et al., 1995; Lee et al., 1998).

In this study, we investigated Hg dynamics within two wetlands in a northern forest ecosystem, evaluating their influence on MeHg production and Hg transport. Both are basin riparian wetlands and potentially influence the fate of Hg inputs from upstream and nearby upland areas. We developed the following hypotheses for this study:

- (a) small flow-through wetlands significantly elevate MeHg concentrations and fluxes in forest streams due to *in situ* MeHg production;
- (b) transformations and transport of Hg in wetlands differ considerably between growing and non-growing seasons; and
- (c) hyporheic exchange enhances the supply of MeHg from wetlands to downstream aquatic ecosystems.

To test these hypotheses we monitored stream water chemistry and hydrology along the main reach of Archer Creek, with sampling locations above, within, and below the study wetlands. Additionally, wetland pore water chemistry was monitored. We evaluated chemical patterns and budgets according to growing and non-growing conditions.

2. Site description

The study site was located in the 3.52 km² Arbutus Lake watershed at the Huntington Wildlife Forest (HWF) in the central Adirondack Mountain region of New York (43°59' N,

74°14' W). The site has long been a focus of biogeochemical studies, notably on sulfur (e.g., Mitchell et al., 1998; David and Mitchell, 1987) and nitrogen dynamics (e.g., Hurd and Raynal, 2004; Bischoff et al., 2001; McHale et al., 2000). A station of the Mercury Deposition Network (MDN) has operated at HWF since 2000. Wet deposition of THg at HWF averaged 7.0 µg/m²-year for the period 2000–2006. Mean annual temperature at the HWF was 4.4 °C. Total annual precipitation during the water year, June 1, 2005 to May 31, 2006, was 1299 mm. The HWF is a northern hardwood forest. 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 are dominated by coarse, loamy, mixed, frigid, Typic Haplorthods in the Becket–Mundal series. The watershed has a mean slope of 11% and a total relief of 225 m (McHale et al., 2004).

Our study site was the primary inlet to the lake, draining the sub-catchment Archer Creek (130 ha), which is gauged with an H-Flume. Approximately 40% of the flow into Arbutus Lake drains from this catchment (Bischoff et al., 2001).

Wetlands cover 4% of the Archer Creek watershed area and are located primarily along the stream channels at lower elevations. Two of the near-stream wetlands, an abandoned beaver meadow (approx. 2 ha) and a riparian peatland (0.5 ha), were chosen for this study. The beaver meadow, which is immediately upstream of the riparian peatland, has been free of beaver activity for about 10–15 years and is devoid of overstory vegetation. Sphagnum moss (*Sphagnum* spp.) and a variety of grasses and sedges are the dominant herbaceous vegetation. Overstory vegetation in the riparian peatland wetland is composed largely of speckled alder (*Alnus incana* ssp. *rugosa*). Herbaceous vegetation in the peatland is dominated by *Sphagnum* spp. and sedges (*Carex* spp.). Soils in the riparian peatland are Greenwood Mucky peat with limited hyporheic exchange flow. Greater hyporheic exchange flow occurs at the beaver meadow where soils are a mixture of Greenwood Mucky peat and hydric soils with high sand content (McHale, 1999). Organic soils in both wetlands range from 1 to 5 m in thickness (McHale et al., 2004). The water table is approximately within 0.05–0.15 m of the wetland surface (McHale et al., 2004, 2000). These two wetlands are representative of the multitude of near-stream wetlands that are found throughout the Adirondack landscape (Wright et al., 2002; Kiernan et al., 2003).

Stream runoff to the beaver meadow is from three sub-catchments (Fig. 1). The main channel, Archer Creek (W9), is an upland catchment and comprises the majority of the runoff input. Additional runoff occurs from two smaller tributaries: a second upland stream (W10) and a stream draining a wetland (W11). A single channel that forms the outflow from the beaver meadow travels approximately 400 m before forming the primary inlet of the riparian peatland (W8). A small rivulet exists at the peatland perimeter, which provides ephemeral flow during snow melt and major storm events (W7). Stream runoff exits the peatland through a single

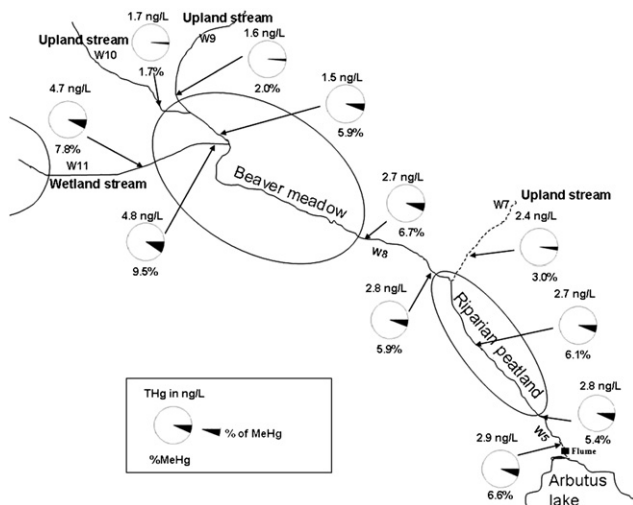


Fig. 1. The percentage of MeHg in THg (% MeHg), indicated by the black pie section, and the THg concentration and the % MeHg, numerically indicated at the top and bottom of each pie, respectively, for each sampling location within the stream reaches of Archer Creek watershed. Stream sampling locations are included for sites sampled during the entire 2-year period.

channel (W5). All streams are perennial at the sampling locations, with the exception of W7 which flows only during high runoff events. Almost all the water passing through the watershed is intercepted by these two wetlands, either as surface water or ground water flow, before draining into Arbutus Lake (McHale et al., 2004). Stream flow within the wetlands is marked by well-defined channels. During winter, the stream flows beneath a thin sheet of ice.

3. Methods

3.1. Stream water and pore water sampling

Stream samples were collected monthly from August 2004 through June 2006 at each of the six different locations, including the inlets and the outlet of each wetland (Fig. 1). Additional stream samples were collected within the wetlands for the first year (August 2004 to August 2005). Stream water results presented in this study represent grab samples and unfiltered Hg analysis. The importance of hydrologic events and dissolved and particulate Hg transport are addressed in a subsequent paper (Bushey et al., submitted).

Wetland pore water samples were collected from Teflon piezometers installed across transects within each wetland. The 2.5 cm diameter pipes were slotted along 8 cm with fine holes (0.0343 cm diameter). A total of 8 piezometers were installed along each wetland transect at four locations and at two depths. Starting in January 2005, pore water was sampled from shallow (20–40 cm) and deep (80–100 cm) zones by pumping into a collection vessel using Teflon tubing and a hand pump. Between each sample, the collection vessel was rinsed with acid (0.04% HCl) followed by milli-Q water to minimize cross-contamination. All samples were collected into acid-cleaned Teflon bottles according to ultra-clean trace metal protocols (EPA, 1996, Method 1669). During sampling, bottles were rinsed thoroughly with sample 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. Pore water samples were filtered using a polyethersulfone (PES) filter (0.45 μm) prior to acid preservation. A second set of stream and pore water samples was collected for ancillary chemical analysis and stored in the dark at 4 °C until analysis. For quality control, field duplicates, trip blank, and field blank samples were included for Hg and ancillary chemistry during every sampling event.

3.2. Chemical analyses

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). A standard calibration was performed before sample analyses. The method detection limit is 0.2 ng/L and 0.02 ng/L for THg and MeHg, respectively. Ancillary water chemistry was analyzed via Standard Methods (APHA/AWWA/WEF, 1998): dissolved organic carbon (DOC), the persulfate-ultraviolet oxidation method (5310C); anions (sulfate, SO_4^{2-} ; nitrate, NO_3^-), ion chromatography with chemical suppression of eluent conductivity (4110 B), and pH by electrometric method (2320). Quality assurance was maintained through duplicate sampling, trip/process blanks, continuous calibration verification (CCV), continuous calibration blank (CCB), 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, including initial and ongoing precision recovery, instrument detection limit, and second source verification, were included to evaluate instrument performance and stability during analysis.

3.3. Hydrologic flux calculations

Stream flow was monitored every 15 min using the H-flume installed at the lake inlet. Stream flow (in mm/month) at other sample locations was prorated based on watershed drainage area. Ground water inflow (mm/month) was estimated as the difference in stream water flow between the inlet and outlet of the wetlands. Fluxes were estimated by multiplying monthly flow (mm/month) by monthly stream water concentration at each sampling location. For the beaver meadow wetland, the fluxes from ground water flow, and each of the three inlets were summed to estimate total influx. Flux calculations were based on water year, defined as the period from 1 June to 31 May (McHale et al., 2000). The dormant season was defined as 1 October to 30 April and growing season as 1 May to 30 September (Mitchell et al., 1996). Fluxes and volume-weighted concentrations of solutes were estimated for the inflow and at the outlet of each wetland for the water year and also for different seasons.

4. Results

4.1. Spatial patterns

Annual discharge for the water year, June 2005 to May 2006, was 748 mm compared to 750 mm for the long-term annual average (1985–1998; Mitchell et al., 2001). Low flow conditions occurred during summer months with relatively dry conditions during summer 2005 from July to September (average discharge at lake inlet was 15 mm/month).

Concentrations of THg and MeHg in stream water draining the upland were low. The mean THg and MeHg concentrations of W9 and W10, which comprise the majority of upland stream flow, were 1.75 and 0.04 ng/L, respectively (Table 1). Noticeable changes in Hg chemistry occurred as the stream drained through the wetland (Fig. 1). Upland stream water inlets (W9 and W10) converge into a single stream immediately after entering the beaver meadow. The % MeHg of these upland inlets W9 and W10 (1.6 and 2% respectively) increased to 6% within the beaver meadow. Stream input W11, which drains an upstream wetland, showed elevated % MeHg (8%) which was further enriched within the beaver meadow (10%; Fig. 1). Within the beaver meadow the upland and wetland inlets mix and emerge as single channel leading to the outlet with elevated % MeHg (6%). Average THg concentrations

Table 1

Average concentrations of THg (ng/L), MeHg (ng/L), DOC (mg/L), and SO₄²⁻ (mg SO₄²⁻/L) in upland and wetland stream waters

Period	Site	THg (ng/L)	MeHg (ng/L)	DOC (mg/L)	SO ₄ ²⁻ (mg/L)
August 2004 to June 2006	Upland	1.75 ± 1.26	0.04 ± 0.03	3.54 ± 1.65	6.13 ± 0.86
	Wetland	3.18 ± 2.33	0.17 ± 0.15	7.62 ± 6.07	5.68 ± 0.87
Growing season	Upland	2.13 ± 1.43	0.04 ± 0.02	4.35 ± 2.11	6.33 ± 0.90
	Wetland	4.38 ± 2.80	0.27 ± 0.16	10.37 ± 7.91	5.56 ± 0.81
Non-growing season	Upland	1.33 ± 0.71	0.02 ± 0.01	3.18 ± 0.85	6.08 ± 1.12
	Wetland	2.37 ± 1.50	0.10 ± 0.09	5.78 ± 0.91	5.79 ± 3.39

Values are shown as average concentration ± one standard deviation. August 2004 to June 2006 represents the entire monthly sampling regime. Average growing season concentrations were calculated from the following months; August to September 2004, June to September 2005, May to June 2006. Average non-growing season concentrations were calculated from the following months; October 2004 to April 2005, October 2005 to April 2006.

of the two upland inlets and one wetland inlet were 1.6, 1.7 and 4.7 ng/L, respectively. The THg concentrations of these streams were not altered substantially following transport through beaver meadow. However, THg concentration at the outlet of the beaver meadow was 2.7 ng/L, a value higher than the upland stream water due to the mixing with the upstream wetland and the supply of THg within the wetland (W11; Fig. 1).

Unlike the beaver meadow, no marked changes were observed in Hg species chemistry during transport through the riparian peatland (Fig. 1). A slight, but not significant, decrease in the % MeHg was noted at the outlet (5.4%) relative to the inlet waters (5.9%).

Annual volume-weighted concentrations of THg, MeHg, and DOC were greater at the outlet of the beaver meadow wetland compared to the inflow values. Slight increases in concentrations were also observed at the outlet of the riparian peatland compared to the inflow (Table 2). Volume-weighted SO₄²⁻ concentrations at the outlet of the wetlands were lower than at the inlet, indicating net SO₄²⁻ retention in the wetlands. Volume-weighted stream concentrations of THg, MeHg, and DOC at the wetlands outlet were greater during the growing

season. Marked increases in volume-weighted MeHg concentration were particularly evident at the outlet (0.23 ng/L) of the beaver meadow compared to the inflow waters (0.08 ng/L; Table 2).

4.2. Temporal patterns

Similar temporal patterns were observed for upland and wetland waters for THg and DOC, though the magnitude of concentrations was distinctively different (Fig. 2). The highest stream concentrations of DOC and THg occurred under the lowest flow conditions during June and July 2005 (Fig. 2). Low flow in combination with more highly reducing

Table 2

Volume-weighted concentrations of THg (ng/L), MeHg (ng/L), DOC (mg/L), and SO₄²⁻ (mg SO₄²⁻/L) during different seasons at the inflow and outlet of beaver meadow and riparian peatland

Period	Site	THg (ng/L)	MeHg (ng/L)	SO ₄ ²⁻ (mg/L)	DOC (mg/L)
Water year (June 2005 to May 2006)	Beaver meadow inflow	2.08	0.05	5.85	4.88
	Beaver meadow outlet	2.64	0.09	5.76	5.92
	Riparian inflow	2.62	0.08	5.75	5.82
	Riparian outlet	2.87	0.09	5.69	6.03
Growing season (June to September 2005, May 2006)	Beaver meadow inflow	2.42	0.08	5.80	5.90
	Beaver meadow outlet	3.90	0.23	5.50	7.97
	Riparian inflow	3.87	0.18	5.46	7.71
	Riparian outlet	3.72	0.21	5.55	7.82
Non-growing season (October 2005 to April 2006)	Beaver meadow inflow	2.00	0.04	5.86	4.63
	Beaver meadow outlet	2.34	0.05	5.82	5.43
	Riparian inflow	2.32	0.05	5.82	5.37
	Riparian outlet	2.66	0.06	5.72	5.61

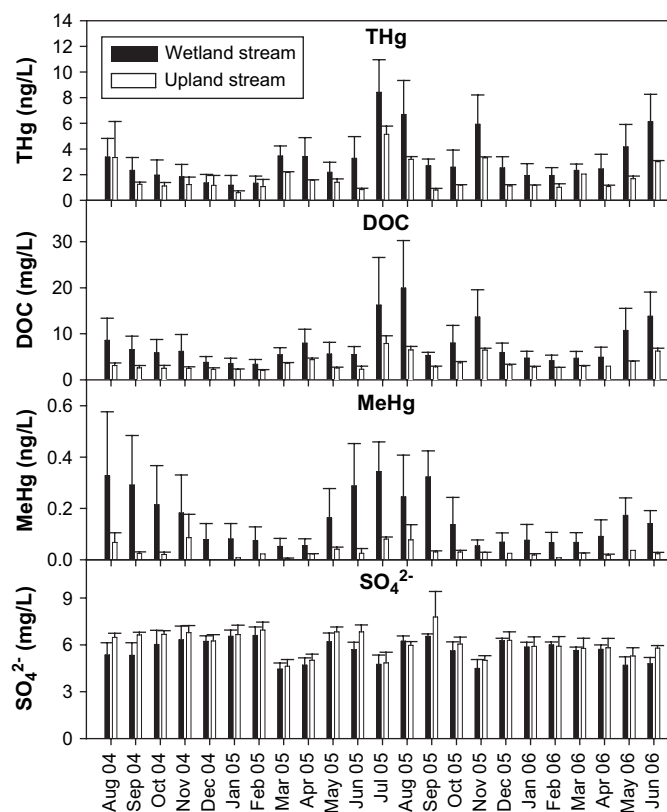


Fig. 2. Mean monthly stream concentrations (not volume weighted) of THg (ng/L), DOC (mg/L), MeHg (ng/L), and SO₄²⁻ (mg SO₄²⁻/L) during the entire study period. Samples have been separated into those collected within wetland (solid bars) and upland (open bars) sites, respectively. Each bar represents the mean (± standard deviation) of all locations.

conditions and higher temperatures in the wetlands during the summer increased the production of DOC. The average concentration of DOC in wetland streams increased almost two-fold during the growing season (10.4 mg/L) relative to the non-growing season (5.8 mg/L; Table 1). In the upland stream, DOC concentrations increased only slightly, from 3.2 mg/L to 4.3 mg/L during the growing season. Elevated discharge that followed dry periods during November 2005 and June 2006 also resulted in elevated concentrations of DOC and THg in stream water (Fig. 2). Although no apparent seasonal patterns were evident, THg closely followed the pattern in DOC concentrations ($r^2 = 0.80$; $\alpha = 0.05$; Fig. 3) highlighting the role of DOC in THg transport at Archer Creek. The strong influence of DOC in the transport of THg has been reported from other studies (e.g., Driscoll et al., 1995; Dennis et al., 2005).

Marked differences in temporal patterns between upland and wetland stream water concentrations was evident for MeHg (Fig. 2). MeHg concentrations in upland stream waters showed little temporal variation and often were near the analytical detection limit. In contrast, large variations with a strong seasonal component were observed for stream MeHg concentrations draining wetlands. Minimum MeHg concentrations in wetland streams were observed during the winter months. MeHg concentrations increased during late spring with the onset of warmer temperatures and peaked during summer. Concentrations of MeHg increased almost three-fold in the wetland streams; from 0.1 ng/L during the non-growing season to 0.3 ng/L during the growing season (Table 1). Comparatively, MeHg concentrations in upland stream water were an order of magnitude lower during both seasons (0.02–0.04 ng/L).

Wetland stream water SO_4^{2-} concentrations were consistently lower than upland streams (Table 1; Fig. 2), indicating reducing conditions and SO_4^{2-} retention in wetlands. Sulfate-reducing bacteria are linked to MeHg production in wetlands (Gilmour et al., 1992; Benoit et al., 2003). The greater difference between upland and wetland stream water SO_4^{2-}

concentrations was consistent with the observation of higher MeHg concentrations draining wetlands during summer months (Fig. 2; Table 1). Note that low SO_4^{2-} concentrations in both upland and wetland streams resulting from snowmelt and high flow rather than reducing conditions during March, April and November 2005 did not coincide with increases in MeHg in stream water.

The increase in MeHg concentrations in wetland stream waters coincided with a decrease in SO_4^{2-} (Fig. 4a). A significant negative correlation existed between MeHg and SO_4^{2-} concentrations during the growing season ($r^2 = 0.28$, $P < 0.0001$), which was not evident for the non-growing season ($r^2 = 0.01$, $P = 0.12$). Decreases in SO_4^{2-} concentrations during the growing season in wetlands is often attributed to dissimilatory SO_4^{2-} reduction (Bailey et al., 1995; Fitzhugh et al., 1999), and has been linked to MeHg production (Branfireun et al., 1999; Gilmour et al., 1998, 1992).

A weak but positive relation was found for DOC and MeHg concentrations (Fig. 4b) during the growing ($r^2 = 0.20$, $P < 0.05$) and non-growing seasons ($r^2 = 0.17$, $P < 0.05$). The slopes of the regressions were similar for the two seasons (Fig. 4b), with the intercept being greater for the growing season.

4.3. Pore water

Pore water concentrations of THg and MeHg varied at different locations within both the beaver meadow and riparian wetlands. However, in both wetlands consistently higher pore water THg and MeHg concentrations were recorded for the shallow depth (20–40 cm) compared to the deeper depth (80–100 cm; Fig. 5). The highest pore water MeHg concentrations were recorded during dry, warm summer months, especially during 2005 (up to 70% of the THg as MeHg). The higher MeHg concentrations in shallow depth pore water were consistent with observations from other studies (Branfireun et al., 1996, 1999). The % MeHg (Fig. 5) in pore water was lower in the shallow depth compared to the deeper depth of the peat due to lower concentrations of THg with depth.

Concentrations of MeHg increased in surface water inlets following drainage through the beaver meadow wetland, suggesting a contribution from pore waters. However, no noticeable changes in MeHg and other species were observed between the inlet and outlet of the riparian peatland. Yet, the MeHg concentrations and the % MeHg in riparian pore waters were comparable to the beaver meadow values (26 vs 29%, respectively). MeHg in pore waters differed considerably between the growing and the non-growing seasons in both wetlands. In comparison to the non-growing season, the growing season MeHg concentrations in shallow depth (20–40 cm) pore waters increased almost two-fold in both wetlands (riparian, 0.27–0.53 ng/L; beaver meadow, 0.33–0.70 ng/L). Similar increases from the non-growing to growing season, but comparatively lower MeHg concentrations were recorded from deeper depth (80–100 cm) (riparian, 0.13–0.33 ng/L; beaver meadow, 0.12–0.26 ng/L). Pore water data do not

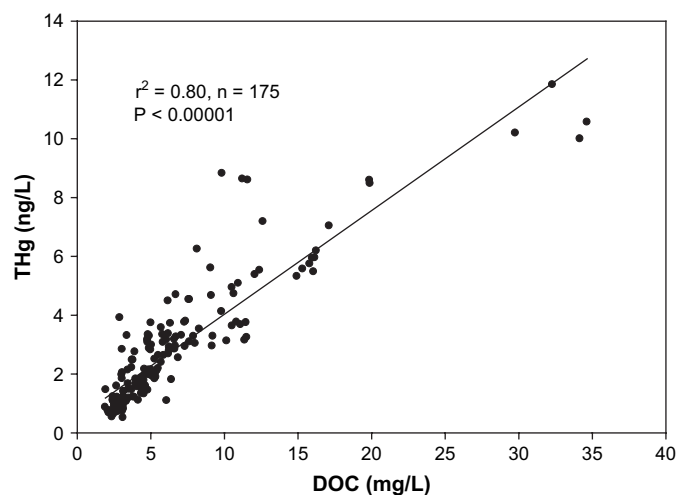


Fig. 3. Concentrations of THg (ng/L) in stream water as a function of DOC (mg/L). Irrespective of season the relationship is significant at $\alpha = 0.05$.

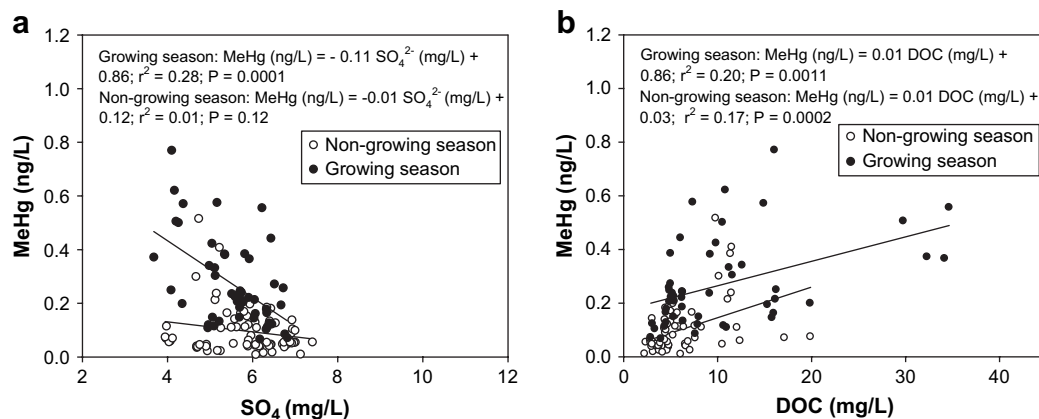


Fig. 4. Regression for MeHg with SO₄²⁻ concentrations in stream water separated by growing and non-growing seasons (a). The relationship between MeHg and SO₄²⁻ is significant during growing season and not during the non-growing season at α = 0.05. Regression for MeHg with DOC concentrations separated by growing and non-growing seasons (b). The relationship is significant (α = 0.05) during both growing and non-growing seasons. Note that the slopes of the regression for the two seasons are nearly parallel.

provide direct evidence of methylation in wetlands. However, high MeHg concentrations and the elevated % MeHg found in pore waters suggest MeHg production in wetland soils, especially at shallow depths.

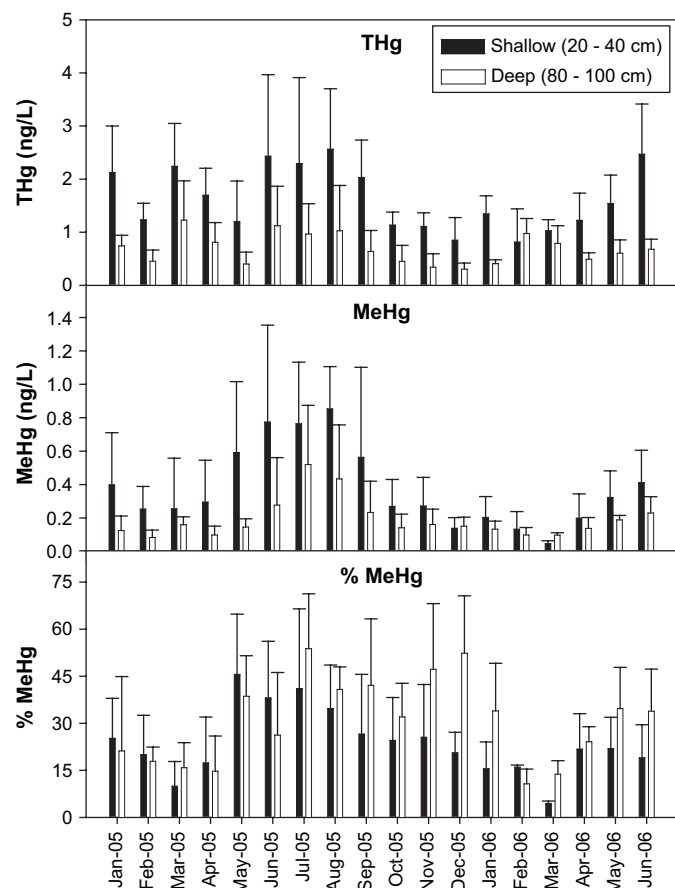


Fig. 5. Average pore water concentrations of THg, MeHg and % MeHg in the riparian and beaver meadow wetlands at shallow (20–40 cm) and deep (80–100 cm) depths. Pore water MeHg was higher at shallow depth compared to deeper depth within both wetlands. Data bars represent average (± standard deviation). With the exception of December 2005 and March 2006, higher concentrations of MeHg were measured at the shallow depth.

4.4. Chemical fluxes

Mass balance calculations show that the beaver meadow was a net source of THg, MeHg and DOC to stream water during different seasons and annually, as evident by the marked differences between respective input and output fluxes (Table 3). In contrast to the beaver meadow, the riparian wetland was a relatively weak to insignificant source of THg, MeHg and DOC. At the outlet of the riparian wetland, the export of THg (1.5 μg/m²-period) and DOC (3.2 g/m²-period) during the non-growing season was three-fold greater compared to that of the growing season (THg; 0.5 μg/m²-period and DOC; 1.3 g/m²-period). The export of MeHg during the non-growing season (0.035 μg/m²-period) was of similar magnitude compared to the growing season (0.029 μg/m²-period). Stream water flux values of SO₄²⁻ from wetlands declined

Table 3
 Fluxes of THg, MeHg, SO₄²⁻ and DOC, during different seasons at the inflow and outlet of beaver meadow and riparian peatland

Period	Site	THg (μg/m ² -period)	MeHg (μg/m ² -period)	SO ₄ ²⁻ (g/m ² -period)	DOC (g/m ² -period)
Water year (June 2005 to May 2006)	Beaver meadow inflow	1.42	0.032	3.99	3.33
	Beaver meadow outlet	1.80	0.059	3.93	4.05
	Riparian inflow	1.86	0.054	4.09	4.14
	Riparian outlet	2.04	0.064	4.05	4.29
Growing season (June to September 2005, May 2006)	Beaver meadow inflow	0.32	0.011	0.76	0.77
	Beaver meadow outlet	0.51	0.030	0.72	1.05
	Riparian inflow	0.53	0.025	0.75	1.05
	Riparian outlet	0.51	0.029	0.76	1.07
Non-growing season (October 2005 to Apr 2006)	Beaver meadow inflow	1.11	0.021	3.23	2.56
	Beaver meadow outlet	1.29	0.029	3.21	3.00
	Riparian inflow	1.33	0.029	3.34	3.08
	Riparian outlet	1.53	0.035	3.29	3.22

markedly ($\sim 0.8 \text{ g/m}^2$ -period) during the growing season compared to non-growing season ($\sim 3.2 \text{ g/m}^2$ -period; Table 3). Annual fluxes for the water year 2005–2006 for THg and MeHg at the outlet of Archer Creek watershed were $2.3 \mu\text{g/m}^2$ -year and $0.092 \mu\text{g/m}^2$ -year, respectively.

5. Discussion

The spatial patterns of stream water indicate that wetlands greatly alter the Hg chemistry of Archer Creek and ultimately Arbutus Lake (Fig. 1). Previous studies of seasonal and temporal Hg dynamics in wetland ecosystems have typically focused on shorter or discontinuous sampling intervals, or were targeted toward rain events and snowmelt (Allan and Heyes, 1998; Shanley et al., 2002; Scherbatskoy et al., 1998). In the current study, continuous monthly monitoring of the wetlands and upland system for 2 years provided an opportunity to examine of seasonal and temporal Hg patterns.

5.1. Total Hg

The range of stream water THg concentrations (0.5 – 11.8 ng/L) from this study was comparable to values reported from other studies (0.01 – 7.4 ng/L , Galloway and Branfireun, 2004; 3.4 – 7.9 ng/L Hurley et al., 1995). Most of the THg in stream water (nearly 75–83%) was in the dissolved phase at Archer Creek (Bushey et al., submitted). Limited particulate Hg and a strong DOC-THg relation (Fig. 3) suggests that transport of THg was primarily driven by DOC supply from this watershed. Organic carbon (OC) substantially influences the hydrological flux of THg in terrestrial watersheds. In some ecosystems DOC has been shown to be the primary carrier of THg (e.g., Driscoll et al., 1995; Allan and Heyes, 1998), while in others, particulate OC (POC; e.g., Kolka et al., 2001) or a combination of both POC and DOC (e.g., Kolka et al., 1999) have been shown to be significant in transport of THg.

Elevated stream water concentrations of THg and DOC occurred during low flow summer months and also during months when high runoff occurred due to wetting events. This pattern reflects DOC controls on THg as a result of two processes; accelerated mineralization during summer months generating ‘high’ DOC and secondly “flushing” of DOC associated with elevated flow conditions (Bushey et al., submitted). The term “flushing” need not necessarily indicate flushing of pore water or contribution from deeper zones of the wetland. The organic rich wetland surface would be sufficient to sustain high DOC and THg concentrations in stream water when these areas are saturated during wetting events.

Hydrologic fluxes were generally higher for THg and DOC during months of elevated discharge, resulting in flow-driven export. Greater than 70% of the annual export of THg and DOC from wetlands occurred during the non-growing season alone. During the non-growing season, the export of THg and DOC from these wetlands was primarily driven by high flow conditions due to snow melt and precipitation events. The well-defined hydrologic flow path in the wetlands facilitated the transport of “flushed” THg and DOC to the stream

during flooding and wetting events. The sensitive response of DOC to discharge at Archer Creek has been reported in other studies (Piatek et al., 2005; Mitchell et al., 2006).

Annual net releases of THg ($0.61 \mu\text{g/m}^2$ -year) and DOC (0.96 g/m^2 -year) occurred from the wetlands, estimated as the difference between the influx to the beaver meadow and outflux from the riparian peatland. Most of the DOC was supplied from the beaver meadow wetland alone (0.72 g/m^2 -year), which has been free of beaver activity for ~ 15 years. Previous studies in the Adirondacks have shown beaver impacted wetlands are important sites of DOC production (Driscoll et al., 1998; Cirimo and Driscoll, 1993). The net production of DOC within the wetlands appears to have resulted in mobilization of THg to surface water as evidenced by the strong THg–DOC relationship (Fig. 3). Other studies have reported wetlands as a net sink of THg, as much as 95% of the input (e.g., Driscoll et al., 1998; St. Louis et al., 1996; Galloway and Branfireun, 2004). However flux calculations reported herein reflect only the hydrologic fluxes. Inputs from atmospheric deposition should also be considered for evaluating the overall source–sink function of THg.

5.2. Methyl Hg

Concentrations of MeHg (0.01 – 0.8 ng/L) from this study were similar to values reported for other wetland ecosystems in the Adirondacks, New York (0.1 – 0.4 ng/L ; Driscoll et al., 1998), Ontario, Canada (0.1 – 0.4 ng/L ; St. Louis et al., 1996; 0.01 – 0.5 ; Galloway and Branfireun, 2004), and Sweden (0.2 – 0.8 ng/L ; Lee et al., 1998, 2000). Maximum concentrations of MeHg occurred during the summer months, coinciding with the peak growing season and the time of maximum decomposition. Other studies have reported elevated MeHg concentrations during the summer months (e.g., Driscoll et al., 1998; Schwesig and Matzner, 2001).

5.3. SO_4^{2-} and methyl Hg

Microbially mediated sulfate reduction results in the production of MeHg in wetlands (Gilmour et al., 1992; Benoit et al., 2003; Gilmour et al., 1998). Our study provides evidence for this mechanism. The difference in SO_4^{2-} concentrations between upland and wetland streams with a nearly three-fold decrease during the growing season compared to the non-growing season (0.8 from $0.3 \text{ mg SO}_4^{2-}/\text{L}$; Table 1) and mass balance calculations (Tables 2, 3) are indicative of sulfate retention in wetlands. A significant inverse relationship was evident for MeHg as a function of SO_4^{2-} during the growing season (Fig. 4a). Sulfate concentrations in pore waters ($2 \text{ mg SO}_4^{2-}/\text{L}$) were low compared to surface water ($6 \text{ mg SO}_4^{2-}/\text{L}$). Coincidentally, MeHg concentrations were high in wetland pore waters with a high % of THg occurring as MeHg (up to 70%).

5.4. Methyl Hg in pore water

In both the riparian and beaver meadow wetlands, pore water MeHg concentrations were higher in the surface shallow

piezometer than at deeper depths (Fig. 5). Branfireun et al. (1996) observed similar results from a peatland, where the highest concentrations of MeHg occurred in “near-surface” peat pore water. Greater inputs of labile carbon, ionic Hg, and nutrient availability, coupled with anoxia, abundance of methylating bacteria, and warmer temperature in the near surface depths would likely sustain higher methylation rates compared to the deeper zones. Although deeper zones of the wetland are likely to experience permanent anoxia, these other conditions are also critical for MeHg production (Branfireun et al., 1996).

5.5. Transport of MeHg

Transport of MeHg in surface water was likely facilitated by DOC. MeHg and DOC exhibited a weak but significant relationship in stream water during both growing and non-growing seasons (Fig. 4b). Both growing and non-growing seasons show an increase in MeHg with a modest increase in DOC (up to 15 mg/L). MeHg concentrations do not continue to increase at elevated DOC (>15 mg/L; Fig. 4b). This pattern suggests that binding to DOC may be limited by the availability of MeHg at high DOC values. We also observed a weak but significant relationship between MeHg and DOC in wetland pore water ($\alpha = 0.05$, $P = 0.001$). Note that the slope of the relationship for pore waters was similar to that observed for stream water (MeHg (ng/L) = $0.01 \times \text{DOC (mg/L)} + 0.13$, $r^2 = 0.18$). MeHg transport by DOC also assumes significance in the context that Hg species were predominantly present in the dissolved phase at Archer Creek (Bushey et al., submitted). The significance of DOC in MeHg transport has been suggested in various other studies (e.g., Allan and Heyes, 1998; Driscoll et al., 1998; Dennis et al., 2005).

Peak concentrations of MeHg during the summer months result from both hydrological processes as well as high MeHg production within wetlands. The summer months are characterized by low flow conditions that increase the residence time of water in wetlands. This condition leads to prolonged interactions and mixing between the stream and wetland pore waters creating favorable circumstances for the supply of MeHg to the stream (Branfireun et al., 2002). During less biologically active periods (non-growing season), lower MeHg production in wetlands coupled with higher discharge resulted in lower MeHg in stream water. Recent studies at Archer Creek identified dilution effects during high flow events on MeHg (Bushey et al., submitted) and SO_4^{2-} (Mitchell et al., 2006), both constituents that are extensively processed biologically.

The estimated annual net export of MeHg from the wetlands ($0.032 \mu\text{g}/\text{m}^2\text{-year}$) was 102% of the input values. High rates of MeHg export from catchments with extensive wetlands have been reported in a number of other studies (e.g., St. Louis et al., 1994; Driscoll et al., 1998). In addition to investigating wetlands as a source of MeHg, we also identified seasonal influences in the transport of MeHg. The growing and non-growing season flux values of MeHg at the outlet of the wetlands were of similar magnitude ($\sim 0.03 \mu\text{g}/\text{m}^2\text{-period}$), and contributed about 50% during each season to the

annual flux value ($\sim 0.06 \mu\text{g}/\text{m}^2\text{-year}$; Table 3). MeHg flux was likely driven by high water yield during the non-growing season, which accounted for most of the annual flux of the other solutes studied (>70% for THg, DOC and SO_4^{2-} ; Table 3). While fluxes of THg, DOC, and SO_4^{2-} declined markedly during the growing season the fluxes of MeHg remained elevated despite a marked decrease in flow. The flux of MeHg during the growing season was clearly due to the elevated MeHg production within wetlands as well as prolonged hydrological interaction of the stream with the wetland under low flow conditions.

MeHg flux at the outlet of the downstream riparian peatland was similar to that at the outlet of the upstream beaver meadow wetland (Table 3). The majority of the MeHg exported from Archer Creek was supplied by the beaver meadow alone due to contributions from wetland pore water. The riparian peatland contributed a small amount ($0.010 \mu\text{g}/\text{m}^2\text{-year}$), less than one-third of the annual net MeHg export ($0.032 \mu\text{g}/\text{m}^2\text{-year}$) in spite of elevated pore water concentrations. The supply of MeHg from the subsurface to surface water was limited due to the hydrologic setting of the riparian peatland as discussed below.

5.6. Hydraulic connectivity of wetlands

Hydrologic flow paths play a critical role in regulating Hg flux from wetlands (St. Louis et al., 1996). Hydraulic conductivity of wetland soil in part, determines the chemical composition of stream water leaving the wetland (McHale et al., 2004; Branfireun et al., 1996). As part of a study in Archer Creek, McHale (1999) compared the extent of the hyporheic zone in the beaver meadow and riparian wetlands. The hyporheic zone in the beaver meadow was comparatively large (extending 7–10 m from the stream channel), facilitating more interaction of stream water with wetland soil. In contrast, subsurface chemical transformations occurring in the riparian peatland were not reflected in stream water. McHale (1999) concluded that the small hyporheic zone and very low hydraulic conductivity of the peat (4.1×10^{-5} to 4.8×10^{-4} m/s) limited stream water interaction with the riparian wetland. Our results are consistent with the observations of McHale (1999). Marked changes in stream water chemistry were observed as the water was transported through the beaver meadow wetland whereas little or no change was observed between the inlet and outlet of the riparian peatland. Subsurface biological and chemical transformations had little impact on the surface water composition draining the riparian peatland. Stream water residence time and length of stream channel are greater in the beaver meadow, affording greater interaction of stream water with the beaver meadow (wetland area ~ 2 ha) compared to the riparian peatland (wetland area 0.5 ha).

5.7. Flux comparison with other studies

The estimated annual MeHg flux for the Archer Creek watershed ($0.092 \mu\text{g}/\text{m}^2\text{-year}$) was within the range of values reported in the literature for other northern wetland influenced watershed ecosystems ($0.03\text{--}0.14 \mu\text{g}/\text{m}^2\text{-year}$; e.g., Povari

and Verta, 2003; Lee et al., 1998, 2000; Hultberg et al., 1995; Krabbenhoft et al., 1995). Wetlands comprise 4% of the Archer Creek watershed. Other watersheds with greater % of wetlands generally have higher MeHg fluxes (0.17–0.55 $\mu\text{g}/\text{m}^2\text{-year}$; e.g., Driscoll et al., 1998; St. Louis et al., 1994; Galloway and Branfireun, 2004). The magnitude of annual THg flux reported from this study (2.3 $\mu\text{g}/\text{m}^2\text{-year}$) is within a wide range of values reported in the literature (0.92–5.9 $\mu\text{g}/\text{m}^2\text{-year}$; e.g., Povari and Verta, 2003; Driscoll et al., 1998; Grigal et al., 2000; St. Louis et al., 1994, 1996; Galloway and Branfireun, 2004; Lee and Hultberg, 1990; Johansson et al., 1991) for forest ecosystems.

6. Conclusions

The role of two small wetlands along the major hydrologic pathway of Archer Creek watershed in controlling Hg dynamics and transport was studied. The wetlands were relatively small landscape units (0.5–2.0 ha) in relation to total watershed area (135 ha). Spatial patterns indicate that the wetlands markedly altered the chemistry of upland stream water by increasing THg, MeHg, DOC and decreasing SO_4^{2-} concentrations. Therefore, the presence of small valley bottom wetlands in forested landscapes is ecologically significant due to the net increase in THg and MeHg transport to downstream aquatic ecosystems. Distinctively high MeHg concentrations in surface waters draining wetlands were evident during the warm summer months when biological activity, SO_4^{2-} reduction and hydrologic residence time were greatest. Elevated MeHg concentrations during the summer months could have implications on Hg bioaccumulation in aquatic organisms, as the runoff from the wetlands represents a major hydrologic input to Arbutus Lake.

Subsurface production of MeHg within the wetlands was evident from the high levels of MeHg and % MeHg detected in wetland pore water. However, the internal hydrology and substrate of the wetlands play a critical role in the supply of MeHg to stream water. Of the two wetlands studied, the riparian peatland is “hydrologically isolated” and therefore did not contribute substantially to the net export of Hg. The beaver meadow had a much stronger hydrologic connection with the stream, enhancing the supply of MeHg to stream water.

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