



## Inputs, storage, and transport of total and methyl mercury in two temperate forest wetlands

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[1] The fluxes and pools of total mercury (THg) and methyl mercury (MeHg) were evaluated for two northern temperate forest wetlands: an abandoned beaver meadow and a riparian wetland. Mass balance calculations reveal that the wetlands are net sources of THg and MeHg, although, the magnitude of the source is a function of wetland connectivity to stream water. The volatilization rate of elemental mercury ( $\text{Hg}^0$ ) in the beaver meadow wetland is of similar magnitude compared to total atmospheric Hg deposition and constitutes an important component of the overall annual Hg budget. In contrast, annual  $\text{Hg}^0$  fluxes exhibited net transfer from the atmosphere to soil at the riparian wetland possibly because volatilization rates were retarded by slower diffusion of  $\text{Hg}^0$  through soil to the air-water interface in water-saturated soil. The storage of THg and MeHg in wetland soil is a large pool which appears coupled with carbon and sulfur accumulation. In the current scenario of decreasing Hg emissions and atmospheric deposition, the large “active” soil pool in wetlands is a potential short-term and long-term source of Hg and MeHg to downstream aquatic ecosystems.

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### 1. Introduction

[2] Mercury (Hg) is a toxic pollutant that is largely released to the environment as a result of anthropogenic activities. The predominant form of Hg in the atmosphere is elemental mercury ( $\text{Hg}^0$ ), which has long residence time and therefore can be transported considerable distance [Schroeder and Munthe, 1998]. Increases in Hg to “environmentally significant” concentrations in remote terrestrial and aquatic ecosystems have been attributed to increases in Hg emissions [Nater and Grigal, 1992; Pilgrim et al., 2000; Fitzgerald et al., 1998]. Archives of historical Hg deposition such as peat cores and lake sediments have provided evidence that elevated Hg accumulation and deposition over the past 100 years is directly related to industrial emissions and human activities [Rood et al., 1995; Engstrom and Swain, 1997]. Geologic Hg sources are generally considered relatively insignificant [Fitzgerald et al., 1998].

[3] Mercury undergoes complex biogeochemical transformations in lake-watershed ecosystems, particularly those with an abundance of wetlands. Wetlands are important in landscapes by converting ionic Hg ( $\text{Hg}^{2+}$ ) inputs from the surrounding uplands and the atmosphere to MeHg. MeHg,

upon transport to adjacent water bodies, strongly bioaccumulates along the aquatic food chain with bioaccumulation factors up to 10 million in piscivorous fish and resulting in elevated exposure to wildlife and humans [Driscoll et al., 2007]. Organic rich wetland sediments with anoxic conditions, nutrient availability and warmer temperature are highly favorable for in situ MeHg production [Gilmour et al., 1992; Hammerschmidt and Fitzgerald, 2004]. Atmospheric deposition of sulfate serves as an electron acceptor for sulfate reducing bacteria, which are thought to largely mediate MeHg production [Benoit et al., 2003]. Wetlands are also important areas of the landscape for the production of dissolved organic carbon (DOC). The transport of Hg species from wetlands is facilitated by DOC supply and binding [Driscoll et al., 1995; Allan and Heyes, 1998; Aiken et al., 2003].

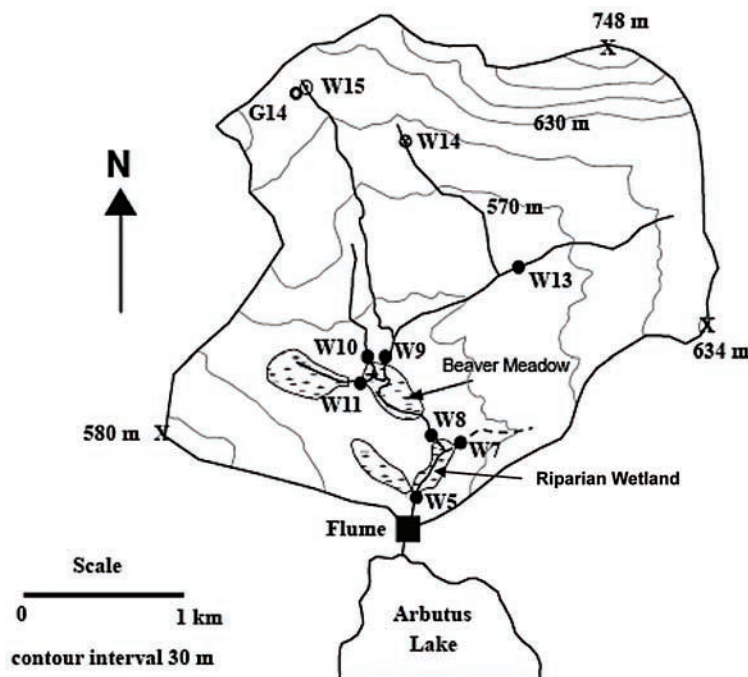
[4] Direct precipitation, dry deposition, throughfall and litterfall are important pathways of Hg inputs and retention in soils [Kolka et al., 1999]. Sequestration of Hg in soil is largely associated with the retention of organic carbon (OC [Grigal, 2003; Nater and Grigal, 1992]). Since OC accumulation is typical in wetlands, the rate of Hg sequestration is thought to be greater in wetlands than upland soils [Grigal, 2003]. Reduced sulfur groups present in OC form stable Hg complexes [Skjyllberg et al., 2003; Lövgren and Sjöberg, 1989]. Therefore, wetland sequestration is an important process that controls overall Hg processing, including methylation, volatilization and transport in stream water [St. Louis et al. 1996; Skjyllberg et al., 2003].

[5] Terrestrial processes can reduce Hg species to  $\text{Hg}^0$ , resulting in volatilization of  $\text{Hg}^0$ . Loss of  $\text{Hg}^0$  to the

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**Figure 1.** Study wetlands, the riparian and beaver meadow, located at the Archer Creek watershed. Stream channel and intensive sampling sites at the inlets and outlet of each wetland are shown by the circles.

atmosphere can occur from vegetation and the soil surface [Erickson and Gustin, 2004; Erickson et al., 2006]. To date, measurements of  $\text{Hg}^0$  volatilization rates have been limited to lakes and upland soil surfaces. The rates of  $\text{Hg}$  volatilization range from  $<5 \text{ ng/m}^2 \text{ h}$  in pristine lakes and forest soils to  $>10,000 \text{ ng/m}^2 \text{ h}$  in contaminated soils [Amyot et al., 2004; Gustin et al., 2003]. Thus, volatilization can be a critical pathway of  $\text{Hg}^0$  loss from ecosystems to the atmosphere. Volatilization processes could also be an important loss mechanism of  $\text{Hg}$  from wetland surfaces. Because wetlands are characterized by saturated surfaces, lower oxidation-reduction potential, and intense biological activity,  $\text{Hg}$  volatilization losses could be higher than upland soils and lakes.

[6] Most previous studies have focused on the drainage export of  $\text{Hg}$  species from wetlands and catchments containing wetlands [Driscoll et al., 1998; Lee et al., 1995; St. Louis et al., 1996; Branfireun et al., 1998]. However, a comprehensive mass balance is needed to improve understanding of  $\text{Hg}$  dynamics in wetlands. In this study we quantify atmospheric deposition, volatilization, and stream inputs and losses, and pools of THg and MeHg in two wetlands. These valley bottom wetlands form the transition zone between the upland and a downstream lake, intercepting majority of the watershed hydrology and therefore substantially influence  $\text{Hg}$  fate and transport.

## 2. Site Description

[7] The study site was located in the  $3.52 \text{ km}^2$  Arbutus Lake watershed at the Huntington Wildlife Forest (HWF) in the central Adirondack Mountain region of New York ( $43^\circ 59' \text{N}$ ,  $74^\circ 14' \text{W}$ ). The site has long been a focus of

biogeochemical research, 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]. Meteorology at the HWF was monitored through the U.S. Environmental Protection Agency (EPA) Clean Air Status and Trends Network (CASTNET; ID-HWF 187). A Mercury Deposition Network (MDN) site has operated at the HWF since 2000. Wet deposition of THg at the HWF averaged  $7.0 \text{ } \mu\text{g/m}^2 \text{ a}$ , where a is years, for the period 2000–2006. Mean annual temperature from 1950 to 1981 was  $4.4^\circ \text{C}$  [Shepard et al., 1989]. Total annual precipitation during the water year, 1 June 2005 to 31 May 2006, was 130 cm. 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].

[8] Our study site was the primary inlet to the lake, draining the subcatchment Archer Creek (130 ha), which is gauged with an H-flume (Figure 1). Approximately 40% of the flow into Arbutus Lake drains from this catchment [Bischoff et al., 2001].

[9] Wetlands cover 4% of the Archer Creek watershed area and are located primarily along the stream channels at lower elevations. Two near-stream wetlands, an abandoned beaver meadow (approximately 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 a 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]. The riparian wetland was highly saturated, with the water table at or above the soil surface, because of beaver activity in late spring 2005 (November). Flooded conditions in the riparian wetland persisted until beaver activity ceased in fall 2006. 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].

### 3. Methods

#### 3.1. Stream and Pore Water

[10] Stream samples were collected monthly from August 2004 through June 2006 at each of the six locations, including inlets and outlet of each wetland (Figure 1). Stream water results presented in this study represent grab samples and unfiltered Hg analysis. 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. One piezometer at each location sampled the 20–40 cm depth and another collocated piezometer sampled the 80–100 cm depth. 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.

[11] All samples were collected into acid-cleaned Teflon bottles according to ultra clean trace metal protocols [Environmental Protection Agency (EPA), 1996]. 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 they 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. Note that a detailed analysis of temporal and spatial patterns of concentrations and fluxes of Hg species in Archer Creek are presented by Selvendiran et al. [2008a] and therefore are not provided here. In this paper, we summarize stream fluxes, with

detailed analysis of deposition and volatilization fluxes, and ecosystem pools of Hg species to complete the wetland Hg mass balances.

#### 3.2. Peat Cores

[12] Peat cores were excavated at two different locations in each wetland using a polyvinyl chloride pipe (2.54 cm ID). The cores, approximately 1 m deep, were sectioned every 3 cm and freeze-dried in the laboratory for 72 h. The weight of the peat sections was noted prior to and after freeze-drying. The freeze-dried samples were stored in acid-cleaned polypropylene containers at room temperature until analysis.

#### 3.3. Vegetation

[13] Herbaceous vegetation within the beaver meadow, including *Sphagnum* spp. and sedges, were sampled at five different locations. Fresh leaf tissues were collected from alder shrubs in the riparian peatland. Leaves were sampled from five individual shrubs during start of the growing season, midgrowing and the end of growing seasons. In addition to alder leaves, *Sphagnum* spp. was also sampled in the riparian peatland. The biomass of foliage in the riparian wetland are as follows: *Alnus incana* is 60 g/m<sup>2</sup>, *Betula alleghaniensis* is 42 g/m<sup>2</sup>, and *Sphagnum* spp. is 95 g/m<sup>2</sup> [Bischoff et al., 2001]. Leaves and herbaceous vegetation were freeze-dried upon arrival in the laboratory or stored at 4°C until freeze-drying. Litter was collected using 0.25 m<sup>2</sup> litter traps that were deployed at four different locations within the riparian wetland. The litter traps were made from treated lumber with a screen bottom. The accumulated litter was collected in brown paper bags and air-dried in a clean environment in the laboratory until analysis.

#### 3.4. Hg Volatilization From Wetlands

[14] Volatilization rates of gaseous Hg were measured using a dynamic flux chamber (DFC) in series with Tekran 1110 synchronized dual-port sampling unit and Tekran automated Hg analyzer [Choi and Holsen, 2008]. Tekran 1110 allows for alternate sampling of ambient air (inlet) and vapor from soil substrate (outlet) within the chamber continuously at a 5 min interval. Hg volatilization flux was estimated on the basis of the following equation:

$$F = (C_{\text{outlet}} - C_{\text{inlet}}) \frac{Q}{A},$$

where  $F$  is flux in ng/m<sup>2</sup> h;  $C_{\text{outlet}}$  and  $C_{\text{inlet}}$  are concentrations of Hg<sup>0</sup> at the outlet and inlet port in ng/m<sup>3</sup>, respectively;  $Q$  is the flushing flow rate through the chamber in m<sup>3</sup>/h; and  $A$  is the surface area of the soil exposed in the chamber in m<sup>2</sup>.

[15] Mercury volatilization flux from the wetland surface was monitored seasonally with respect to various environmental conditions (e.g., ambient temperature, humidity, solar radiation, soil temperature) from fall 2005 to fall 2006. During each sampling, volatilization fluxes were measured continuously for a 24-h period to characterize diurnal patterns. For quality assurance, manual injections of Hg in ambient air, soil vapor and Tekran analyzer were performed before and after data collection.

### 3.5. Chemical Analyses

[16] THg was analyzed via oxidation, purge and trap, and cold vapor atomic fluorescence spectroscopy (CVAFS [EPA, 2002]). MeHg was analyzed via distillation, aqueous ethylation, purge and trap, and CVAFS (modified to 90 mL of sample [EPA, 2001]). The method detection limit is 0.2 ng/L and 0.02 ng/L for THg and MeHg, respectively. Ancillary water chemistry was analyzed following *Clescerl et al.* [1998], including dissolved organic carbon (DOC), the persulfate-ultraviolet oxidation method (5310C), sulfate ( $\text{SO}_4^{2-}$ ), ion chromatography with chemical suppression of eluent conductivity (4110 B); and pH electrometric method (2320).

[17] Total Hg in peat was measured directly using a LECO<sup>®</sup> AMA 254 Advanced Mercury Analyzer to a reporting limit of 4 ng/g. Approximately 0.1 g of sample was combusted in the presence of pure oxygen, followed by amalgamation, thermal desorption and detection by atomic absorption spectroscopy (AAS). Coal fly ash (NIST SRM 1655b) and estuarine sediment (CRM 580, Certified Reference Material) were used as standard reference materials. MeHg in peat was analyzed by microwave assisted acid extraction followed by ethylation, purge and trap and CVAFS detection [Tseng et al., 1997]. Approximately 1 g of homogenized sediment sample was dissolved in 10 ml of 2N nitric acid solution in a Teflon extraction tube. The extraction tubes were exposed to microwave irradiation at 200 W for 5 min (Milestone ETHOS TC advanced microwave laboratory). After irradiation, the contents were transferred to 15 ml vials and centrifuged for 8 min at 5000 rpm. The supernatant was transferred into 15 ml vials for analysis. CRM 580 was used as a standard reference material for the analysis. We also analyzed total nitrogen (N), total sulfur (S) and total carbon (C) composition in peat cores with an Elemental Combustion System, Model ECS 4010 (Costech Analytical Technologies, Valencia, California, USA). Note that peat cores are highly acidic and total C is virtually all organic.

[18] Total Hg in leaf tissue and litter samples was analyzed sequentially using a DMA-80 Direct Mercury Analyzer (Milestone, Microwave Laboratory Systems, Shelton, CT) utilizing thermal decomposition, catalytic reduction, amalgamation, desorption, and detection by AAS. Apple leaf (NIST SRM 1515; National Institute of Standards and Technology, Gaithersburg, MD, 44.0 ng/g THg) was used as the standard reference material.

[19] MeHg in leaf tissue and litter samples were analyzed via alkaline digestion followed by ethylation, purge and trap in according with EPA method 1630 [EPA, 2001]. Approximately 20 mg of tissue were digested for 24 h in 3 ml of 25% KOH in methanol at 55°C [Hintelmann and Nguyen, 2005]. The digest (300  $\mu\text{l}$ ) was diluted in 50 ml of water and analyzed for MeHg. The analytical detection limit for this method was 0.64 ng/g.

[20] A standard calibration was performed before sample analyses. 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, SRM, CRM, MS, and MSD) for Hg and ancillary chemical analyses. For MeHg

analysis in leaf and litterfall samples, the recoveries from SRM ranged between 85 and 118%. 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.

### 3.6. Fluxes and Pool Size

[21] Streamflow was monitored every 15 min using the H-flume installed at the lake inlet. Streamflow (in mm/month) at other sample locations was prorated on the basis of watershed drainage area. Groundwater 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. Monthly discharge rates were applied for flux calculations. Measured concentrations of throughfall [Choi et al., 2008] and stream water were multiplied by precipitation quantity and discharge rate, respectively, and summed over the interval of interest to estimate fluxes. Litter fluxes were based on measured concentrations, the accumulated litter mass and surface area of the litter traps. Fluxes were estimated on the basis of growing and nongrowing seasons. The dormant season was defined as 1 October through 30 April and growing season as 1 May through 30 September.

[22] Wet THg deposition was obtained from the MDN site at the HWF. Dry deposition was estimated as 26% of wet THg deposition at the HWF [Selvendiran et al., 2008b]. Wet deposition (1999–2000) of MeHg was 0.55% of the THg wet deposition at HWF [Lindeman, 1996]. We applied the same ratio for estimating wet MeHg deposition in this study.

[23] Total annual input was estimated as the sum of hydrologic, litterfall, and throughfall fluxes. Total annual output includes hydrologic and net volatilization losses. Retention coefficient ( $R$ ) was estimated as follows:

$$R = (\text{Input} - \text{Output}) / \text{Input}.$$

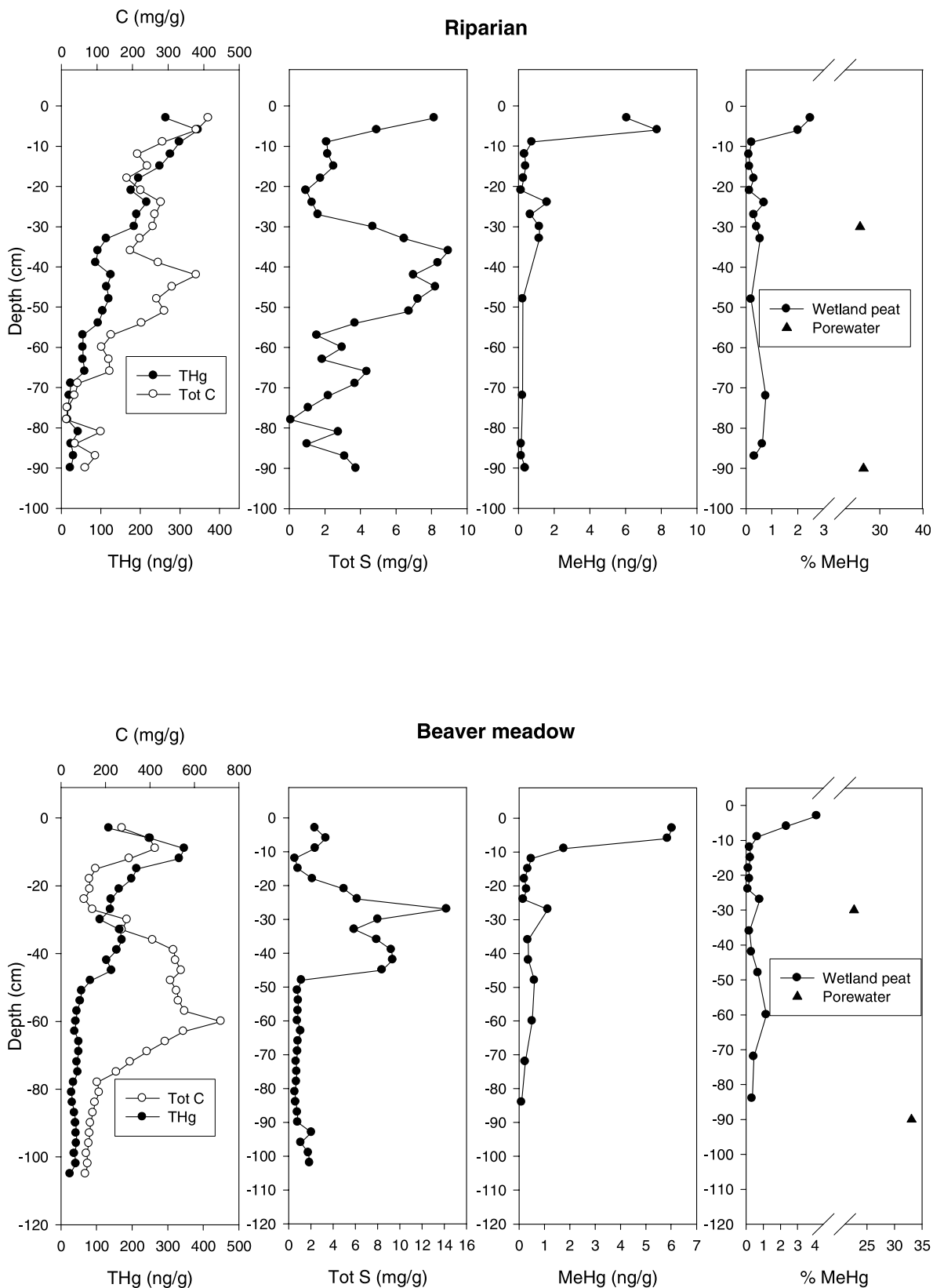
The retention coefficient represents the proportion of the incoming mass that was retained within the wetlands. A negative value for  $R$  implies that the output exceeds the input and the wetland is a source. To obtain percent retention the value of  $R$  was multiplied by 100.

[24] Soil pools of THg and MeHg for individual peat sections were based on measured concentrations, the bulk density and depth. The resulting values from individual sections were summed to estimate total pool of Hg in peat up to 1-m depth. Vegetation Hg pools was estimated on the basis of measured concentrations and dry weight of vegetation species [Bischoff et al., 2001].

## 4. Results

### 4.1. Peat Characteristics

[25] In both the riparian and beaver meadow wetlands, the highest concentrations of THg were found near the surface of the peat deposits, within the top 15 cm (Figures 2a and 2b). The average THg concentration in the top 15 cm of the soil was similar at the riparian (287 ng/g) and beaver



**Figure 2.** Concentrations of THg, total C, total S, MeHg, and percent MeHg as a function of peat depth at (top) riparian wetland and (bottom) beaver meadow wetland. Note that the corresponding percent MeHg in pore water (triangles) at an average depth of 30 and 90 cm are shown for comparison.

**Table 1.** Element Ratio of THg and MeHg to Total C in the Riparian, Beaver Meadow, and Upland Soils<sup>a</sup>

	Element	Element Ratios		
		Riparian	Beaver Meadow	Upland
Active pool (<15 cm)	ng THg/g C	983 ± 234	876 ± 350	15,546 ± 5222
	ng MeHg/g C	10 ± 10	13 ± 16	94 ± 16
Less active pool (>15 cm)	ng THg/g C	553 ± 230	381 ± 393	28,719 ± 11,618
	ng MeHg/g C	5 ± 4	1 ± 2	85 ± 53
Total (~100 cm)	ng THg/g C	624 ± 279	453 ± 421	23,596 ± 16,614
	ng MeHg/g C	6 ± 5	3 ± 7	89 ± 35

<sup>a</sup>Values represent average ratio ± standard deviation in active pool (<15 cm), less active pool (>15 cm), and total soil profile up to 1-m depth. Carbon content in the wetland soil is high compared to upland soils. Consequently, there is more Hg per unit C in the upland soil. The upland soil data are from C. T. Driscoll (unpublished data, 2008), with the forest floor representing the active soil pool and the mineral soil the less active pool.

meadow (256 ng/g) wetlands. THg concentrations generally decreased with depth and declined as much by tenfold (23 ng/g) in the maximum depths sampled (90–110 cm). In the riparian wetland, a sharp decline in THg was observed in a sand lens between 30 and 40 cm (Figure 2a). THg concentrations followed a pattern of total carbon (total C) in the riparian wetland ( $r = 0.67$ ). In contrast, THg was not correlated with C in the beaver meadow wetland over the entire profile ( $r = 0.07$ ). However, strong Hg-C patterns were observed in the upper 30 cm of the peat at both riparian ( $r = 0.58$ ) and beaver meadow sites ( $r = 0.60$ ). In both wetlands the primary peak in total C occurred within the upper 10 cm of the soil. A secondary peak was observed for total C at 40–80 cm depth (42 cm at riparian and 60 cm at beaver meadow sites; Figures 2a and 2b). The Hg/C ratio varied with peat depth with the highest values at the surface peat and values decreasing with depth. The total S concentrations also showed an enrichment at the peat surface. However, peak concentrations were observed at 20–40 cm depth, likely reflecting historical patterns atmospheric S deposition (Figures 2a and 2b). The average total S concentrations were  $3.8 \pm 2.6$  and  $3.1 \pm 3.5$  mg/g respectively, at the riparian and beaver meadow sites. Organic S groups were not characterized in this study. However, previous studies have shown that soil S at the HWF is largely associated with C-bonded S [David and Mitchell, 1987] we hypothesize that organic S functional groups within the OM control the binding of Hg.

[26] Concentrations of MeHg in peat averaged  $1.36 \pm 2.24$  and  $1.24 \pm 1.96$  ng/g respectively, at the riparian and beaver meadow sites. In both wetlands, high MeHg concentrations were found at the near surface peat (0–6 cm; average  $6.44 \pm 0.89$  ng/g) and decreased markedly with depth (9–90 cm; average  $0.54 \pm 0.45$  ng/g). The % MeHg in peat varied by 1 order of magnitude with depth from up to 4% at the top 6 cm to an average of 0.4% for the remaining 90 cm. Average MeHg concentration of pore water at the riparian and beaver meadow at shallow depth (0.38 and 0.47 ng/L, respectively; 20–40 cm) was twofold higher compared to values at greater depths (0.21 and 0.18 ng/L, respectively; 80–100 cm). However, the % MeHg in pore waters at the shallow and deeper depths were comparable at riparian site (25 versus 26%) and different at the beaver meadow (23 versus 33%). Elevated % MeHg in deeper pore water in both wetlands was most likely due to removal of  $\text{Hg}^{2+}$  from the solution phase with depth.

[27] Because of variation of Hg with depth, we define the upper 15 cm of the peat profile as the active pool, where

processing and availability of Hg species is greatest, and the remainder of the profile as the less reactive, less mobile pool of Hg and MeHg. In both wetlands, concentrations of Hg and MeHg in solid and solution phase were highest within the active pool compared to deeper depth (>15 cm). The ratio of Hg and MeHg to C was substantially higher in the active pool compared to the less active pool (Table 1). Surface enrichment of S and MeHg in the upper peat is also suggestive of wetland S retention and MeHg production in the upper peat by biological processes.

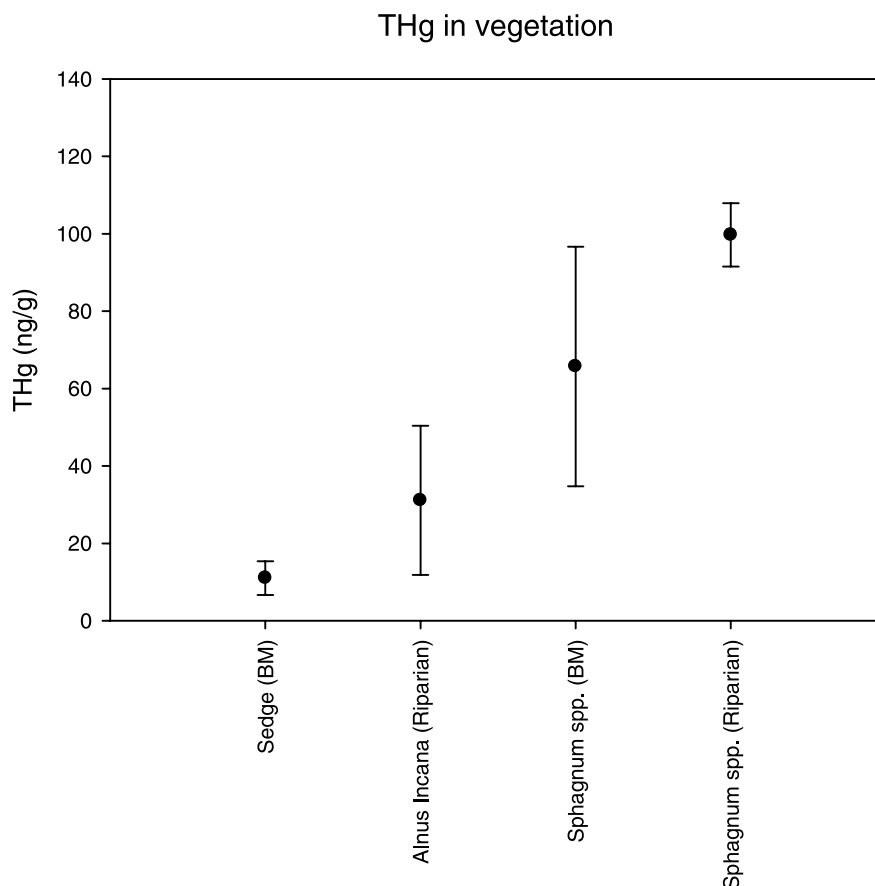
#### 4.2. Hg in Vegetation

[28] The THg content varied considerably among different vegetation species in the wetlands (Figure 3). Concentrations of THg in plant materials varied in the following order:  $11.01 \pm 4.4$  ng/g in sedges (*Carex* spp.)  $<31.1 \pm 19.3$  ng/g in alder leaf tissue (*Alnus incana*)  $<77.0 \pm 30.1$  ng/g in moss (*Sphagnum* spp). Considerable spatial variations were observed in THg concentrations in *Sphagnum* moss at the beaver meadow ( $99.7 \pm 8.2$  ng/g) and particularly at the riparian wetland ( $65.7 \pm 30.9$  ng/g).

[29] Concentrations of THg in fresh leaf tissue of alder showed annual as well as interannual variation from leaf out to senescence (Figure 4). Initial THg concentration during the start of the growing season (June) was  $6.6 \pm 1.1$  ng/g, and increased tenfold by the end of growing season (October;  $61.1 \pm 13.6$  ng/g). Periodic sampling was carried out in 2006 during the start of growing season (2 June), midgrowing season (25 July) and the end of growing season (16 September). Regression analysis on 2006 data ( $\alpha = 0.05$ ;  $P < 0.0001$ ) indicates the THg accumulation rate of  $0.29$  ng/g d in alder from leaf out to senescence.

[30] Concentrations of THg in leaf litter during the 2004, 2005, and 2006 showed limited annual variation ( $47.6 \pm 3.0$ ,  $46.2 \pm 1.7$  and  $45.7 \pm 5.1$  ng/g respectively). In addition to alder leaves, leaf litter was also composed of other species including yellow birch, red spruce and red maple. THg concentration in composite leaf litter was slightly lower than the peak concentrations in alder leaf tissue that were observed by the end of growing season. Average annual leaf litter mass in the riparian wetland was  $130.2$  g/m<sup>2</sup> [Bischoff et al., 2001], resulting in an annual litterfall THg deposition of  $6.0$  μg/m<sup>2</sup> a.

[31] The MeHg content of alder leaf tissue and litterfall were close to the analytical detection limit. The average MeHg content of alder over the growing season was  $0.27 \pm 0.17$  ng/g ( $n = 6$ ). Litterfall MeHg content was  $0.56 \pm 0.43$  ng/g ( $n = 3$ ); twofold greater than in fresh leaf. The



**Figure 3.** Concentration of THg (ng/g, dry weight) in different plant material at beaver meadow (BM) and riparian wetlands. Error bars represent maximum and minimum values.

percent MeHg content in alder (0.9%) and litterfall (1.2%) was consistent with previous studies (1.5% [Grigal, 2003]).

### 4.3. Net Volatilization of Hg<sup>0</sup> From Wetlands

#### 4.3.1. Beaver Meadow

[32] At the beaver meadow, air-soil exchange of Hg<sup>0</sup> (20-min resolution) showed marked diel patterns and seasonal variations (Figure 5). Soil moisture during spring season was high because of snowmelt. Because of a prolonged precipitation event (0.7 mm/h) on 12 May 2006 (spring), the wetland soil had high antecedent moisture conditions prior to measurements during 13 May. A rain event also occurred during the course of the measurements on 14 May. Net volatilization of Hg<sup>0</sup> was observed initially during the daytime following increases in solar radiation (SR), and ambient air temperature (AAT) and decreases in percent relative humidity (RH). However, daytime fluxes following rain event and nighttime fluxes were negative, indicating net transfer of Hg<sup>0</sup> from air to soil (Figure 5). The average net soil flux of Hg<sup>0</sup> for the 24-h period during spring was  $-0.8 \pm 0.9$  ng/m<sup>2</sup> h (SR =  $54 \pm 42$  w/m<sup>2</sup>; AAT =  $9.1 \pm 0.4$ °C; RH =  $88.4 \pm 4\%$ ).

[33] Air-surface exchange of Hg<sup>0</sup> exhibited a different diel pattern during summer (July 2006) when the wetland surface exhibited dry conditions. The predominant flux during summer was the net volatilization of Hg<sup>0</sup>. Nighttime volatilizations were considerably lower than daytime fluxes (Figure 5). The average net volatilization Hg<sup>0</sup> flux during

summer was  $2.1 \pm 2.9$  ng/m<sup>2</sup> h (SR =  $103 \pm 101$  w/m<sup>2</sup>; AAT =  $21.4 \pm 4.7$ °C; RH =  $68.5 \pm 22\%$ ).

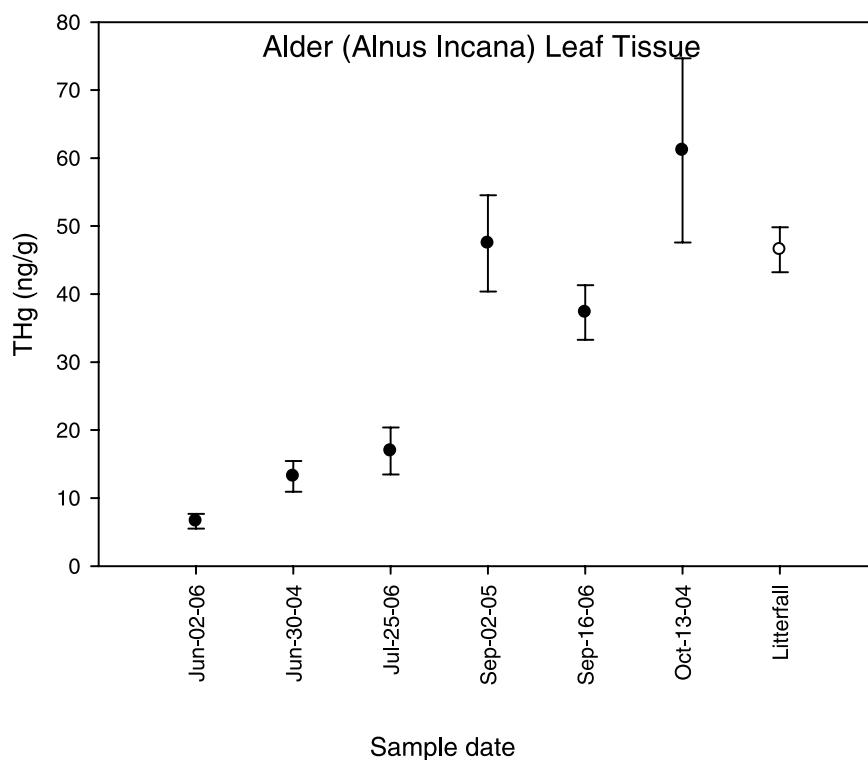
[34] Diel patterns during fall (October 2006) were characterized by maximum Hg<sup>0</sup> volatilization during daytime. Whereas, minimum Hg<sup>0</sup> fluxes ranging from net volatilization to net transfer to soil occurred during night (Figure 5). The average net Hg<sup>0</sup> flux observed during fall was  $0.81 \pm 2.1$  ng/m<sup>2</sup> h. (SR =  $62 \pm 70$  w/m<sup>2</sup>; AAT =  $3.5 \pm 5.4$ °C; RH =  $89.4 \pm 5.8\%$ ).

#### 4.3.2. Riparian

[35] Because of flooding of the riparian wetland, saturated conditions existed during seasonal measurements in spring, summer and fall of the year 2006. Flux measurements under these conditions indicated no net volatilization, but rather predominantly a net transfer of Hg<sup>0</sup> from the atmosphere to the wetland soil during spring ( $-1.3 \pm 1.4$  ng/m<sup>2</sup> h), summer ( $-3.9 \pm 1.9$  ng/m<sup>2</sup> h) and fall ( $-3.6 \pm 1.1$  ng/m<sup>2</sup> h). Therefore, the riparian wetland was a net sink of Hg<sup>0</sup> under the saturated conditions that occurred. In contrast, flux measurements during drier conditions on summer 2005 (September), prior to the onset of beaver activity, showed an average net Hg<sup>0</sup> volatilization flux of  $3.8 \pm 2.5$  ng/m<sup>2</sup> h. Ancillary meteorological parameters (SR, AAT, and RH) were not available during summer 2005 measurements.

### 4.4. Annual Hg<sup>0</sup> Flux Estimates

[36] The field flux measurements were used to estimate the magnitude of seasonal and annual Hg<sup>0</sup> fluxes from



**Figure 4.** Patterns in THg in alder leaf tissue in riparian wetland over the 2004, 2005, and 2006 growing seasons. Average THg in litterfall collected toward the end of 2004, 2005, and 2006 growing seasons is shown for comparison. Error bars represent maximum and minimum values.

wetlands. Because of snow cover in the wetlands, volatilization flux was assumed to be zero during winter (December–February). Measured seasonal net  $\text{Hg}^0$  fluxes were prorated for the growing and nongrowing season. At riparian site, the fluxes were net transfer of  $\text{Hg}^0$  to the soil during growing ( $11 \mu\text{g}/\text{m}^2$ ) and nongrowing seasons ( $4.6 \mu\text{g}/\text{m}^2$ ). At beaver meadow, the estimated net  $\text{Hg}^0$  fluxes were net volatilization from soil during the growing ( $4.6 \mu\text{g}/\text{m}^2$ ) and slight net volatilization during nongrowing season ( $0.01 \mu\text{g}/\text{m}^2$ ). The cumulative annual  $\text{Hg}^0$  fluxes were net transfer from air to soil ( $15.6 \text{mg}/\text{m}^2 \text{a}$ ) at the riparian and net volatilization at the beaver meadow sites ( $4.6 \text{mg}/\text{m}^2 \text{a}$ ). Measured net  $\text{Hg}^0$  fluxes did not correlate with any of the ancillary variables (SR, AAT, RH, soil temperature) and therefore a predictive empirical model for  $\text{Hg}^0$  volatilization/deposition was not developed from this study.

#### 4.5. Wetland Compartment Pools

[37] The storage of THg in soil of the riparian wetland was  $30 \text{mg}/\text{m}^2$  (calculated to 90 cm depth) compared to  $19.6 \text{mg}/\text{m}^2$  in the beaver meadow (calculated to 102 cm depth). The active pool (calculated for the upper 15 cm) of THg represented 27% of the total storage for both riparian ( $8.15 \text{mg}/\text{m}^2$ ) and beaver meadow ( $5.3 \text{mg}/\text{m}^2$ ) wetlands. Therefore, in both wetlands the less active pool of THg was large and about 73% of the total soil storage (Table 2).

[38] The total soil pool of MeHg in the riparian wetland was  $214 \mu\text{g}/\text{m}^2$ , with about 30% in the active pool (upper 15 cm to  $64 \mu\text{g}/\text{m}^2$ ). The soil storage of MeHg was about threefold lower in beaver meadow wetland ( $81 \mu\text{g}/\text{m}^2$ ) than the riparian wetland. Unlike the riparian wetland, the soil

MeHg storage in beaver meadow was about equally divided between the active ( $41.6 \mu\text{g}/\text{m}^2$ ) and less active pool ( $39.6 \mu\text{g}/\text{m}^2$ ).

[39] In the riparian wetland, the estimated THg pool in overstory foliage was  $3.08 \mu\text{g}/\text{m}^2$ , including *Alnus incana* ( $1.85 \mu\text{g}/\text{m}^2$ ) and *Betula alleghaniensis* ( $1.23 \mu\text{g}/\text{m}^2$ ). The estimated MeHg storage in overstory foliage was  $0.03 \mu\text{g}/\text{m}^2$ . The other dominant foliage type, *Picea* spp., was not considered in this study. Therefore, the estimate of Hg storage in foliage was an underestimate. The storage of THg in *Sphagnum* spp., the predominant understory vegetation, was  $9.48 \mu\text{g}/\text{m}^2$ .

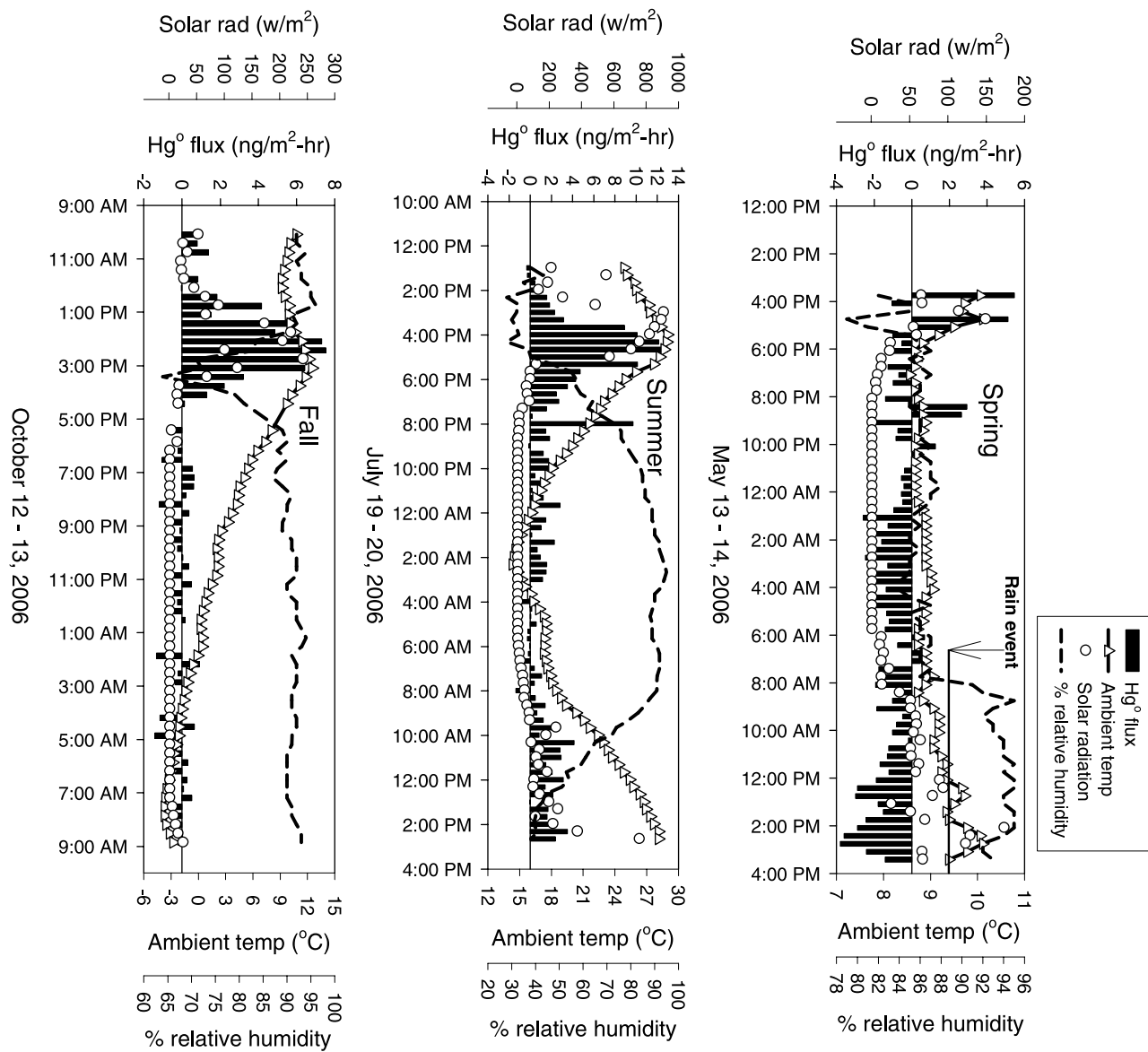
[40] Beaver meadow is devoid of overstory vegetation. Because of lack of information on biomass, understory vegetation pools were not estimated for this wetland.

#### 4.6. Fluxes and Mass Balances

[41] Average Hg fluxes were estimated during growing and nongrowing season for the 2-year duration of the study (Table 3). Annual and seasonal Hg fluxes and mass reported herein represent the average of the 2 years unless mentioned otherwise. Note that areal fluxes are expressed on the basis of per unit area of wetland.

##### 4.6.1. Beaver Meadow Wetland

[42] Total atmospheric deposition flux (wet + dry) of THg to beaver meadow was  $8.8 \mu\text{g}/\text{m}^2 \text{a}$ , equivalent to a total mass input of  $0.18 \text{g}/\text{a}$ . An amount equal to one half of the atmospherically deposited THg ( $0.09 \text{g}/\text{a}$ ) was lost via volatilization at a rate of  $4.7 \mu\text{g}/\text{m}^2 \text{a}$ . Runoff inputs from uplands supplied  $0.6 \text{g}/\text{a}$  of THg, which corresponds to an areal flux of  $27.5 \mu\text{g}/\text{m}^2 \text{a}$ . Drainage losses of THg from the



**Figure 5.** Diel patterns in  $\text{Hg}^0$  flux, solar radiation, ambient air temperature, and percent relative humidity from beaver meadow wetland during spring, summer, and fall 2006. A rain event was encountered during spring 2006 field measurements, and the duration of the rain event is indicated. Rain events resulted in negative  $\text{Hg}^0$  flux values.

wetland was 2.2 g/a or an areal flux of  $108.2 \mu\text{g}/\text{m}^2 \text{ a}$ . Annually, a net release of THg (1.5 g/a), about 211% of the total input, occurred from the wetland.

[43] Direct wet MeHg deposition to the wetland surface was estimated as 0.8 mg/a corresponding to an areal flux of  $0.04 \mu\text{g}/\text{m}^2 \text{ a}$ . Water inflow supplied 0.01 g/a of MeHg from the upland to the wetland (areal flux:  $0.03 \mu\text{g}/\text{m}^2 \text{ a}$ ). Comparatively, an eightfold increase in areal flux ( $3.73 \mu\text{g}/\text{m}^2 \text{ a}$ ) and total mass flux (0.075 g/a) of MeHg was observed at the outflow of the wetland (Table 3). The net release of MeHg from the beaver meadow wetland (0.06 g/a) was 623% of the total input.

[44] The Hg fluxes of the beaver meadow wetland exhibited clear seasonal variations. Rates of total atmospheric deposition and particularly net  $\text{Hg}^0$  volatilization fluxes were substantially greater during the growing season

compared to the nongrowing season (Table 3). THg fluxes due to inflow and outflow were greater during the nongrowing season compared to growing season (Table 3). However, MeHg fluxes due to inflow and outflow during the growing season were similar to those during the nongrowing season, suggesting that both biological processes and water flows are important controllers of MeHg concentrations in stream water (Table 3).

#### 4.6.2. Riparian Wetland

[45] Monthly throughfall measurements (January 2005 through December 2007 [Choi *et al.*, 2008]) at the upland deciduous plot were applied to the riparian wetland. The cumulative annual throughfall flux of THg during August 2005 through July 2006 was  $7.3 \mu\text{g}/\text{m}^2 \text{ a}$ . The mass flux of THg resulting from throughfall deposition was 0.04 g/a. Litterfall deposition of THg was 0.03 g/a at an areal flux of

**Table 2.** Storage of THg and MeHg in the Riparian, Beaver Meadow, and Upland Soils<sup>a</sup>

	Element	Pool ( $\mu\text{g}/\text{m}^2$ )		
		Riparian	Beaver Meadow	Upland
Active pool (<15 cm)	THg	8150 $\pm$ 650	5294 $\pm$ 580	13,492 $\pm$ 4327
	MeHg	64 $\pm$ 13	42 $\pm$ 6	98 $\pm$ 30
Less active pool (>15 cm)	THg	21,884 $\pm$ 422	14,350 $\pm$ 495	50,927 $\pm$ 5727
	MeHg	150 $\pm$ 3	40 $\pm$ 1	162 $\pm$ 39
Total (100 cm)	THg	30,034 $\pm$ 534	19,644 $\pm$ 538	64,420 $\pm$ 8205
	MeHg	214 $\pm$ 6	81 $\pm$ 3	260 $\pm$ 33

<sup>a</sup>Storage of THg and MeHg were estimated for the active pool, less active pool and total soil profile up to 1-m depth. The upland soil data are from C. T. Driscoll (unpublished data, 2008), with the forest floor representing the active soil pool and the mineral soil the less active pool.

6.0  $\mu\text{g}/\text{m}^2$  a. The total direct deposition (throughfall and litterfall) of THg to riparian wetland (13.3  $\mu\text{g}/\text{m}^2$  a) was 1.6-fold greater than the value for beaver meadow wetland (8.6  $\mu\text{g}/\text{m}^2$  a). The annual net transfer of  $\text{Hg}^0$  from the atmosphere to soil (15.6  $\mu\text{g}/\text{m}^2$  a), estimated from seasonal  $\text{Hg}^0$  measurements, was approximately twice as much as the combined inputs of THg from throughfall and litterfall (Table 3). Stream water draining the upstream beaver meadow forms the inflow to the riparian wetland. The areal flux rate of THg in runoff inflow (449.7  $\mu\text{g}/\text{m}^2$  a) was similar to the value at the outflow of the wetland (507.5  $\mu\text{g}/\text{m}^2$  a). The mass flux of THg at the outflow (2.5 g/a) was slightly greater than the inflow value (2.2 g/a). Mass balance indicates an annual net release of THg (0.14 g/a) from riparian wetland of about 6% of the total input; much lower in magnitude compared to beaver meadow.

[46] The throughfall MeHg flux of 0.04  $\mu\text{g}/\text{m}^2$  a was estimated by applying a MeHg/THg ratio of 0.55% that was observed in wet deposition. Litterfall flux of MeHg to the forest floor was 0.07  $\mu\text{g}/\text{m}^2$  a; approximately 60% of the total direct deposition input (throughfall and litterfall, 0.11  $\mu\text{g}/\text{m}^2$  a). The areal flux of MeHg from the watershed runoff was 13.9  $\mu\text{g}/\text{m}^2$  a. The mass flux of MeHg from

watershed runoff (0.07 g/a) was more than 2 orders of magnitude greater than the mass of MeHg supplied from total MeHg deposition input (throughfall and litterfall, 0.5 mg/a). The export of MeHg via outflow was 0.08 g/a corresponding to an areal flux rate of 15.1  $\mu\text{g}/\text{m}^2$  a. The annual net release of MeHg from the riparian wetland was 0.01 g/a or 8% of the total input.

[47] THg deposition flux during the growing season (throughfall and  $\text{Hg}^0$  transfer to soil, 15.7  $\mu\text{g}/\text{m}^2$ ) was slightly greater than the value during the nongrowing season (throughfall and litterfall and  $\text{Hg}^0$  transfer to soil, 13.2  $\mu\text{g}/\text{m}^2$ ). Compared to beaver meadow site, the THg deposition at the riparian wetland was 1.6-fold greater during the growing season and 3.8-fold greater during the nongrowing season. However, runoff fluxes of THg and MeHg differed only marginally at the inlet and outlet of the riparian site during both growing and nongrowing seasons (Table 3).

#### 4.7. $\text{SO}_4^{2-}$ Mass Balance

[48] The direct atmospheric deposition of  $\text{SO}_4^{2-}$  to the wetlands was a small fraction of the total input (<2% of total input). Terrestrial runoff was the dominant source of  $\text{SO}_4^{2-}$  inputs to beaver meadow (4 g/m<sup>2</sup> a;  $1.8 \times 10^3$  kg) and

**Table 3.** Average Annual and Seasonal Areal Fluxes and Total Mass Budgets of THg and MeHg at the Riparian and Beaver Meadow Wetlands During the Period August 2004 to July 2006<sup>a</sup>

Transport Process	THg ( $\mu\text{g}/\text{m}^2$ )			MeHg ( $\mu\text{g}/\text{m}^2$ )			THg (g)			MeHg (g)		
	G	NG	A	G	NG	A	G	NG	A	G	NG	A
<i>Beaver Meadow</i>												
Wet Deposition	4.23	2.74	6.97	0.023	0.015	0.038	0.085	0.055	0.139	0.0005	0.0003	0.0008
Dry Deposition	1.10	0.71	1.81	NA	NA	NA	0.022	0.014	0.036	NA	NA	NA
Net Volatilization	4.64	0.01	4.65	NA	NA	NA	0.093	0.0002	0.093	NA	NA	NA
Water Inflow	10.05	17.41	27.46	0.20	0.28	0.48	0.20	0.35	0.55	0.004	0.006	0.010
Water Outflow	43.01	65.18	108.19	2.01	1.72	3.73	0.86	1.30	2.16	0.04	0.03	0.07
$\Sigma$ Input – $\Sigma$ Output	–32.27	–44.33	–76.60	–1.79	–1.42	–3.21	–0.65	–0.89	–1.53	–0.04	–0.03	–0.06
Percent retention							–210	–213	–211	–807	–484	–623
<i>Riparian</i>												
Throughfall	4.64	2.67	7.31	0.026	0.015	0.040	0.02	0.01	0.04	0.0001	0.0001	0.0002
Litterfall		5.97	5.97	NA	0.090	0.090	NA	0.03	0.03	NA	0.0004	0.0004
Net Volatilization	–11.02	–4.58	–15.6	NA	NA	NA	–0.06	–0.02	–0.08	NA	NA	NA
Water Inflow	172.24	277.49	449.73	7.29	6.59	13.87	0.86	1.39	2.25	0.036	0.033	0.069
Water Outflow	191.76	315.71	507.47	7.91	7.20	15.11	0.96	1.58	2.54	0.040	0.036	0.076
$\Sigma$ Input – $\Sigma$ Output	–3.86	–25.00	–28.86	–0.60	–0.53	–0.13	–0.02	–0.13	–0.14	–0.003	–0.003	–0.006
Percent retention							–2	–9	–6	–8	–8	–8

<sup>a</sup>Here G and NG correspond to fluxes during growing and nongrowing seasons, respectively. A represents the annual average value. Percent retention was estimated as the difference between total input and total output over total input and multiplying the value by 100. Negative values for net volatilization indicate net transfer of  $\text{Hg}^0$  from the atmosphere to soil. Water inflow and inflow represent sources from both surface and groundwater. Note that MeHg fluxes associated with in situ methylation and demethylation were not evaluated in this study.

riparian wetlands ( $4.1 \text{ g/m}^2 \text{ a}$ ;  $4.9 \times 10^3 \text{ kg}$ ). Drainage losses of  $\text{SO}_4^{2-}$  exceeded the total inputs at the beaver meadow site ( $3.8 \text{ g/m}^2 \text{ a}$ ;  $4.7 \times 10^3 \text{ kg}$ ). In contrast, net retention of  $\text{SO}_4^{2-}$  occurred at riparian wetland as the drainage losses ( $3.7 \text{ g/m}^2 \text{ a}$ ;  $4.7 \times 10^3 \text{ kg}$ ) were lower than the total input.  $\text{SO}_4^{2-}$  plays complex role in Hg processing in wetlands.

## 5. Discussion

[49] The range of THg (16–347 ng/g) and MeHg (0.1–7.8 ng/g) concentrations in wetland soil in this study were within the ranges of values reported from other studies [Steinnes and Sjøbakk, 2005; Liu et al., 2003; Schwesig and Matzner, 2000; Branfireun and Roulet, 2002]. In both the riparian and beaver meadow wetlands THg concentrations were relatively stable below certain depths (>55 cm). The elevated concentrations and the strong Hg-C relationship in the upper peat are indicative of accumulation of nongeologic THg and likely reflect the legacy of historical atmospheric Hg deposition. The nearly identical patterns in THg and total C in topsoil layers of the riparian and beaver meadow wetlands suggest that most of the accumulated Hg from atmospheric deposition is associated with organic matter, probably with reduced organic S functional groups [Skylberg et al., 2003]. Also note that the peaks in THg in the active pool were preceded by depletion of THg at the surface peat, particularly at the beaver meadow wetland (Figures 2a and 2b). Possible explanations for this depth pattern include drainage and volatilization losses of THg.

[50] The enrichment of S in the surface peat (active pool) in both wetlands can influence Hg dynamics (Figures 2a and 2b). The cycling of S in the active pool can increase the availability of  $\text{SO}_4^{2-}$ , which can serve as an electron acceptor for SRB and enhance methylation. Notable differences were also observed in the total S concentrations in the active pool of the wetlands, with higher concentrations in riparian wetland (4 mg/g) than the beaver meadow (1.9 mg/g). The soil storage (up to 1-m depth) of S at the riparian site ( $1155 \text{ g/m}^2$ ) was also substantially greater than at beaver meadow ( $441 \text{ g/m}^2$ ). Consistent with these observations, mass balance calculations indicate that the riparian wetland exhibits net  $\text{SO}_4^{2-}$  retention and the beaver meadow net  $\text{SO}_4^{2-}$  loss.

[51] The peat concentration profiles illustrate near surface accumulation of MeHg (top 10 cm), most likely due to in situ methylation, as other sources including direct atmospheric deposition and watershed drainage inflow are minor inputs (see Table 3). The abundance of  $\text{SO}_4^{2-}$ , labile organic C, warm temperature, and the presence of oxic-anoxic interface due to water table fluctuations at the wetland surface result in optimal conditions for MeHg production [Branfireun et al., 1999; Verta et al., 1994].

[52] Soil water MeHg concentration in the uplands at the HWF are near detection limits (<2% of the THg concentrations) (C. T. Driscoll, personal communication, 2008). In contrast, the average MeHg concentration in wetland pore waters was approximately 25% of THg (Figures 2a and 2b), with values increasing during summer up to 70% [Selvendiran et al., 2008a]. The maximum MeHg concentration in the shallow pore water (~–30 cm) in this study (1.6 ng/L) was low compared to values reported for similar

wetland types in Canada (2.4–7 ng/L [Branfireun and Roulet, 2002; Branfireun et al., 1996]). In our study, maximum soil MeHg appeared within 10 cm of the wetland surface (Figures 2a and 2b). If we were able to sample pore waters near the surface of the water table, MeHg concentrations would likely have been higher, for the reasons listed above. The production and accumulation of MeHg in the near surface zone of the wetland has implications for transport in surface waters. Upland runoff composition (low MeHg) from the watershed was markedly altered, with an increase in the supply of MeHg as the water drains through the wetlands [Selvendiran et al., 2008a].

[53] We hypothesize that the majority of Hg is bound to C. The abundance of Hg-complexing carbon can be illustrated by the Hg/C element ratio. Comparison of Hg/total C ratio in soil among landscape units at the HWF indicates that uplands have the ability to sequester more THg and MeHg per unit carbon than wetlands (Table 1). The THg/C and MeHg/C ratios in upland soils are more than 1 order of magnitude greater compared the values in wetlands soil. However, the average concentration (1-m depth) of total C in wetland soil (198 mg/g in riparian; 308 mg/g in beaver meadow) was more than 1 order of magnitude greater than the upland soil (4 mg/g). Therefore, higher total C in wetland soils suggests that there are more total binding sites for Hg species and hence the lower Hg/total C ratios compared to the upland soils at the HWF. The mobility of THg and MeHg in uplands is limited despite the higher Hg/total C ratio. The transport of Hg and MeHg in surface water at the HWF was primarily facilitated by DOC; DOC accounts for >85% of total organic carbon in Archer Creek stream water [Bushey et al., 2008a; Selvendiran et al., 2008a]. Concentrations of DOC, THg and MeHg in stream water draining the upland landscape were low compared to the marked increase in concentrations of these species within the wetland landscape [Selvendiran et al., 2008a]. DOC and Hg concentrations in wetland streams were also found to be seasonally variable with peaks during warmer season coinciding with periods of higher microbial activity. The C rich nature of the soil substrate, the saturated conditions which result in incomplete microbial mineralization of C, and the relatively abundant, mobile DOC in wetland soils combine to enhance transport of Hg to surface waters.

[54] The concentrations and pattern of THg in wetland vegetation (sedges < foliage < *Sphagnum*) were consistent with the literature [Liu et al., 2003; Hall and St. Louis, 2004]. Spatial difference in moss THg was observed between riparian (mean 100 ng/g) and beaver meadow (mean 67 ng/g) wetlands. Liu et al. [2003] suggested that THg in moss is predominantly derived from direct atmospheric deposition due to the absence of a vascular cylinder. Because of litterfall delivery, direct deposition of Hg was greater at the riparian wetland compared to the beaver meadow. However, stream water and volatilization losses of THg were not significant at the riparian site (Table 3). Therefore, the concentration of THg in *Sphagnum* likely reflects differences in the magnitude of deposition inputs and losses in these wetlands and is consistent with differences between these wetlands in the concentrations of THg at the peat surface (upper 6 cm; 306 ng/g at riparian, 193 ng/g at beaver meadow).

[55] The rate of THg accumulation in the alder leaves over the growing season (0.29 ng/g d) was similar to the values reported for deciduous vegetation in the uplands at the HWF (0.22–0.35 ng/g d [Bushey et al., 2008b]). Soil uptake of Hg by roots is thought to be negligible [Bishop et al., 1998; Bushey et al., 2008b, Rea et al., 2002]. Therefore uptake of gaseous Hg<sup>0</sup>, controlled by stomata, is likely the predominant pathway of Hg accumulation in foliage [Ericksen et al., 2003]. In addition to the atmosphere, soil emissions could potentially be an important source of Hg<sup>0</sup> for accumulation in foliage. Reemission of Hg<sup>0</sup> from foliage to the atmosphere has also been reported [Ericksen and Gustin, 2004; Lindberg, 1996]. Therefore accumulation is the mass of THg remaining after net exchange of Hg<sup>0</sup> across the foliage-air barrier. Litterfall THg in the riparian wetland (46.5 ± 3.3 ng/g) was similar to values reported for the uplands at the HWF (47–62 ng/g [Bushey et al., 2008b]) and hardwood species from other studies (42 ng/g [St. Louis et al., 2001] and 36 ng/g [Rea et al., 2002]).

[56] The hourly average net Hg<sup>0</sup> air/soil exchange fluxes observed in wetlands from this study (2.9 up to –3.9 ng/m<sup>2</sup> h) were within the range, albeit on the low end, of reported values for remote upland forested soils (0.1–2.7 ng/m<sup>2</sup> h [Ericksen et al., 2006], 2.95 ng/m<sup>2</sup> h [Poissant and Casimir, 1998], 0.2–1.6 ng/m<sup>2</sup> h [Choi and Holsen, 2008], and 11 ng/m<sup>2</sup> h [Grigal, 2002]). The estimated annual rates of Hg<sup>0</sup> volatilization from beaver meadow wetland (4.7 μg/m<sup>2</sup> a) was similar in magnitude compared to the values reported for the uplands (6.8 μg/m<sup>2</sup> a [Choi and Holsen, 2008]) and Arbutus Lake surface (8.4 μg/m<sup>2</sup> a [Selvendiran et al., 2008b]) at the HWF.

[57] Volatilization of Hg<sup>0</sup> can be a loss of “new Hg,” derived from atmospheric deposition, or “old Hg,” derived from the soil substrate. The controls on soil Hg volatilization are complex and the controlling environmental variables likely include solar radiation, soil and air temperature, humidity, precipitation, soil wetness and soil Hg concentration [Carpi and Lindberg, 1998; Gustin et al., 1997; Rasmussen et al., 1998; Choi and Holsen, 2008; Ericksen et al., 2006]. However, the mechanism of Hg volatilization from soils and the controlling factors under different environmental conditions remain unclear. In this study the measured Hg<sup>0</sup> fluxes varied greatly both spatially and temporally. Therefore, Hg<sup>0</sup> fluxes carry the highest uncertainty among all of the fluxes reported in this study.

[58] We observed virtually no Hg<sup>0</sup> volatilization when the riparian wetland soil surface was saturated. The direction of fluxes indicates a net transfer of Hg<sup>0</sup> from the atmosphere to the soil (–1.8 up to –3.9 ng/m<sup>2</sup> h) under these conditions. Corresponding to these fluxes, the annual rate of net transfer of Hg<sup>0</sup> from the atmosphere to soil was high (up to 16 μg/m<sup>2</sup> a; Table 3). Our findings of Hg behavior under saturated conditions hold implications for overall Hg budget and warrants further study under similar conditions in other wetlands.

[59] Studies have shown that water addition to dry soil resulted in an immediate release of Hg<sup>0</sup> [Gustin and Stamenkovic, 2005; Lindberg et al., 1999]. It was hypothesized that physical displacement of Hg<sup>0</sup> in soil pores by water contributes to this pattern [Lindberg et al., 1999]. However, negative flux values have been reported in a few other studies following precipitation events [Choi and

Holsen, 2008] and under saturated conditions [Gustin et al., 2006]. The volatilization mechanism is a three step processes involving reduction of Hg<sup>2+</sup> to Hg<sup>0</sup> and diffusion of Hg<sup>0</sup> to the surface followed by diffusion across the soil-air boundary [Wallschlager et al., 2000; Grigal, 2002]. Although saturated conditions favor reduction reactions, the latter steps involving diffusion pathway of Hg<sup>0</sup> may be limited by the presence of water. Poissant and Casimir [1998] suggested that the presence of water results in different diffusion characteristics and requires larger activation energy for Hg volatilization reactions to occur. In addition to limiting Hg<sup>0</sup> diffusion, the presence of dissolved oxidants in water may increase the potential for oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup>. Alternatively, biological process may be important in driving net transfer of Hg<sup>0</sup> to soil (i.e., bacterial oxidation of Hg<sup>2+</sup> to Hg<sup>0</sup>) under saturated conditions. In general under saturated conditions soil Hg volatilization are suppressed and did not exhibit the typical diel patterns (Figure 5) [Gustin and Stamenkovic, 2005; Gustin et al., 2006]. Note that the pattern of net transfer of Hg<sup>0</sup> from the atmosphere to soil at the riparian wetland is likely a transient phenomenon associated with the flooding of this site by beaver activity.

[60] Wet deposition flux of THg from the current study (7.0 μg/m<sup>2</sup> a) was within the range of values reported for the northeastern U.S. (3.8–12.6 μg/m<sup>2</sup> a [Driscoll et al., 2007]). Throughfall flux of THg was similar to the value reported for a deciduous forest at Sunday Lake watershed (7.4 μg/m<sup>2</sup> a [Demers et al., 2007]), which is in close proximity (80 km west) to the HWF. THg flux from litterfall was more than twofold lower in the wetland (6.0 μg/m<sup>2</sup> a) compared to the uplands at HWF (17 μg/m<sup>2</sup> a) because of greater input of litter mass to the upland forest floor. Annual export of THg on a watershed area basis (2.3 μg/m<sup>2</sup> a) and MeHg (0.1 μg/m<sup>2</sup> a) in stream water are consistent with the range of values reported for northern forest catchments containing wetlands (THg, 1.0–3.4 μg/m<sup>2</sup> a; MeHg, 0.01–0.2 μg/m<sup>2</sup> a [St. Louis et al., 1996; Grigal et al., 2000]).

[61] The storage of Hg in vegetation (THg, 0.001–0.009 mg/m<sup>2</sup>; MeHg, 0.03 μg/m<sup>2</sup>) was negligible compared to storage in wetland soil (THg, 20–30 mg/m<sup>2</sup>; MeHg, 81–214 μg/m<sup>2</sup>). Researchers have reported that the storage of Hg in aboveground biomass is 2–3 orders of magnitude lower compared to soil storage [Schwesig and Matzner, 2000; Grigal et al., 2000]. Soil Hg storage was considerably greater in the riparian wetland (THg, 30 mg/m<sup>2</sup>; MeHg, 214 μg/m<sup>2</sup>) compared to the beaver meadow wetland (THg, 20 mg/m<sup>2</sup>; MeHg, 81 μg/m<sup>2</sup>). Higher soil Hg storage in the riparian wetland can be explained by the differences in the physical characteristics between the two wetlands. The presence of overstory vegetation has enhanced the direct Hg deposition inputs to the riparian wetland. In addition in a previous study we observed, on the basis of a fluvial mass balance, there was little net production/loss of Hg species in the riparian wetland (Table 3 [Selvendiran et al. 2008a]). This behavior was due to limited hyporeheic exchange between the stream and the wetland. Our study indicates saturated conditions retarded Hg<sup>0</sup> volatilization; and the riparian wetland is subject to frequent flooding and saturated conditions. In addition, the bulk density of peat is higher in riparian wetland (8.7 ± 7.5 g/cm<sup>3</sup>) compared to beaver

meadow ( $3.1 \pm 1.5 \text{ g/cm}^3$ ). Therefore, higher inputs, minimal hydrologic export and lower volatilization have resulted in greater soil Hg storage in riparian wetland compared to beaver meadow wetland.

[62] The residence time (residence time = pool/total inputs) of THg in the active pool (upper 15 cm) is on the order of 260 and 360 years in the riparian and beaver meadow sites respectively. Whereas the residence time of MeHg in the active pool was 2 years in the riparian wetland and 3 years in the beaver meadow wetland. The large storage of THg in wetlands and its mobility is an issue of interest. Assuming stable export rate of Hg in runoff, the active soil pool will likely continue to be a major long-term source of THg contamination in remote wetland dominated aquatic ecosystems.

## 6. Conclusions and Implications

[63] Wetlands at the HWF, although much smaller in landscape units compared to the upland area, are zones of high Hg fluxes. The net fluxes of Hg and MeHg per unit area of wetland were much greater than upland values. For total Hg, drainage fluxes dominate. For MeHg, in-wetland production dominated for the beaver meadow, while drainage inflow dominated the riparian wetland. Hg mass balances indicate that wetlands were net sources of total and MeHg. Previous studies have demonstrated that wetlands are source of MeHg, but rather a sink for THg [e.g., Driscoll et al., 1998; Grigal et al., 2000]. However, Hg<sup>0</sup> volatilization/deposition fluxes were not accounted in mass balances in these studies. Hg<sup>0</sup> volatilization/deposition in wetland was an important flux, but is also the highly variable with large uncertainty. The soil pool is a source of Hg species to stream water through DOC binding [Selvendiran et al., 2008a]. Therefore, wetlands could potentially serve as a long-term source of THg, regardless of industrial Hg emission reductions, because of large storage of THg in wetland soil. However, reduction in industrial Hg emissions and deposition could limit the supply of Hg available for the production of MeHg in wetlands. The very short residence time of MeHg in the active upper zone of peat suggests that MeHg production, demethylation, and transport could be very responsive to changes in inputs of Hg<sup>2+</sup> and/or SO<sub>4</sub><sup>2-</sup>. These conclusions about MeHg, while strongly support by the data presented here, are speculative, as in situ methylation/demethylation were not measured. Percent wetland coverage and proximity of wetlands to streams are important landscape characteristics that influence Hg export from watersheds [Kolka et al., 1999; Driscoll et al., 1995]. However, mass balances indicate that in addition to proximity (e.g., beaver meadow), Hg export from wetlands is also limited by the connectivity of the wetland to stream water (e.g., riparian wetland).

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