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Total mercury and methylmercury dynamics in upland–peatland watersheds during snowmelt

**Carl P. J. Mitchell · Brian A. Branfireun ·
Randall K. Kolka**

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Abstract Wetlands, and peatlands in particular, are important sources of methylmercury (MeHg) to susceptible downstream ecosystems and organisms, but very little work has addressed MeHg production and export from peatland-dominated watersheds during the spring snowmelt. Through intensive sampling, hydrograph separation, and mass balance, this study investigated the total mercury (THg) and MeHg fluxes from two upland–peatland watersheds in Minnesota, USA during the 2005 spring snowmelt and proportionally attributed these fluxes to either peatland runoff or upland runoff. Between 26% and 39% of the annual THg flux and 22–23% of the annual MeHg flux occurred during the 12-days snowmelt study period, demonstrating the importance of large hydrological inputs to the annual mercury flux from these watersheds. Upland and peatland runoff were both important sources of THg in watershed export. In contrast to other research, our data show that peatland pore waters were the principal source of MeHg to watershed export during snowmelt. Thus, despite cold and mostly frozen surface conditions during the snowmelt period, peatland pore waters continued to be an important source of MeHg to downstream ecosystems.

Keywords Dissolved organic carbon · Mercury · Methylmercury · Peatland · Snowmelt · Watershed hydrology

Abbreviations

CVAFS	Cold vapor atomic fluorescence spectroscopy
DOC	Dissolved organic carbon
HDPE	High density polyethylene
MeHg	Methylmercury
MDN	Mercury Deposition Network
MEF	Marcell Experimental Forest
NADP	National Atmospheric Deposition Program
Q	Discharge
SWE	Snow water equivalent
THg	Total mercury

Introduction

Mercury is a potent neurotoxin (Ratcliffe et al. 1996) and human exposure to mercury is primarily through

C. P. J. Mitchell · B. A. Branfireun
Department of Geography, University of Toronto,
3359 Mississauga Road North, Mississauga, ON,
Canada L5L 1C6

C. P. J. Mitchell (✉)
Department of Physical and Environmental Sciences,
University of Toronto at Scarborough, 1265 Military
Trail, Toronto, ON, Canada M1C 1A4
e-mail: carl.mitchell@utoronto.ca

R. K. Kolka
Northern Research Station, U.S. Department of
Agriculture Forest Service, 1831 Highway 169 East,
Grand Rapids, MN 55744, USA

the consumption of contaminated fish (Clarkson et al. 2003). Although inorganic mercury (Hg^0 and Hg(II)) in the atmosphere is the principal non-point source of mercury to “pristine” ecosystems (Fitzgerald et al. 1998), it is the transformation of inorganic mercury into methylmercury (MeHg), an organic form that accumulates in aquatic biota (Bloom 1992), that is of greatest concern. Since atmospheric sources of MeHg constitute a minor input of MeHg into most lakes and wetlands, intra-watershed transformations of Hg(II) to MeHg predominate (Rudd 1995; Sellers et al. 2001). A thorough understanding of where Hg is methylated within the watershed and when areas of MeHg production are connected to susceptible aquatic ecosystems is critical to understanding the effects of atmospheric Hg deposition and how MeHg enters the food chain.

Wetlands have been shown to be important sources of MeHg to downstream aquatic ecosystems (St. Louis et al. 1994; Branfireun et al. 1998, 2005). Mercury methylation is closely linked to microbial sulfate reduction (Gilmour et al. 1992) and mercury methylation occurs in wetlands because of anaerobic conditions that favor sulfate reduction (Branfireun and Roulet 2002). Much of this research has taken place during the growing season. The role of wetlands in MeHg production and export during strong hydrological inputs such as spring snowmelt remains unclear.

Several studies have investigated the flux of total mercury (THg) and/or MeHg from a variety of watersheds, both those with wetlands (St. Louis et al. 1994, 1996; Bishop et al. 1995; Driscoll et al. 1998; Kolka et al. 1999, 2001; Loseto et al. 2004) and those without (Scherbatskoy et al. 1998; Balogh et al. 2000). Much of this research has demonstrated the importance of dissolved organic carbon (DOC) and particulate matter as vectors for mercury transport (Driscoll et al. 1995; Kolka et al. 1999). However, very little intensive research has been conducted to investigate the importance of snowmelt to annual THg and MeHg fluxes even though the annual hydrographs of northern watersheds are normally dominated by spring snowmelt. For example, a single high-flow event and transport with organic material were important mechanisms of THg flux in a Vermont forest, with up to 50% of the annual THg flux occurring at the onset of snowmelt runoff (Scherbatskoy et al. 1998). Few studies have investigated both MeHg and wetlands in addition to THg. Two studies, which have monitored MeHg export from watersheds containing wetlands over the snowmelt period, have concluded that MeHg in melting snow was an important source of MeHg in watershed export (Bishop et al. 1995; Loseto et al. 2004). To the best of our knowledge, we are unaware of similarly intensive research undertaken in the temperate or boreal regions of North America. It is thus not well-known here whether wetlands continue to be important sources of MeHg during cold periods or whether MeHg exported during the snowmelt period is mostly derived from the melting snowpack. Furthermore, understanding the hydrological sources of inorganic Hg in runoff is potentially very important. Although it is currently unknown whether more recent sources of Hg to the environment (i.e., in melting snow) are more bioavailable to methylating bacteria than the existing Hg pool (i.e., in soil water), understanding the source attribution could be an initial step into such an investigation.

In this study, we have investigated THg and MeHg fluxes during the spring snowmelt in two small upland–peatland watersheds in Minnesota and considered their relative importance in the annual mass balance. Through sampling of various watershed compartments and separation of the watershed hydrograph into upland and peatland components, we have attempted to parse out the important source areas for export of THg and MeHg to downstream aquatic ecosystems during this hydrologically important period of time.

Methods

Study sites

This study was undertaken in two peatland-dominated watersheds (S2 and S6) at the Marcell Experimental Forest (MEF) in north-central Minnesota (47° 32′ N, 93° 28′ W), USA (Fig. 1). Watershed S2 has a 3.0 ha central bog surrounded by 6.2 ha of forested upland. Watershed S6 has a 2.4 ha central bog complex (1.5 ha bog + 0.9 ha lagg) surrounded by 6.5 ha of forested upland. MEF is an operating site of both the National Atmospheric Deposition Program (NADP) and the Mercury Deposition Network (MDN). Thus,

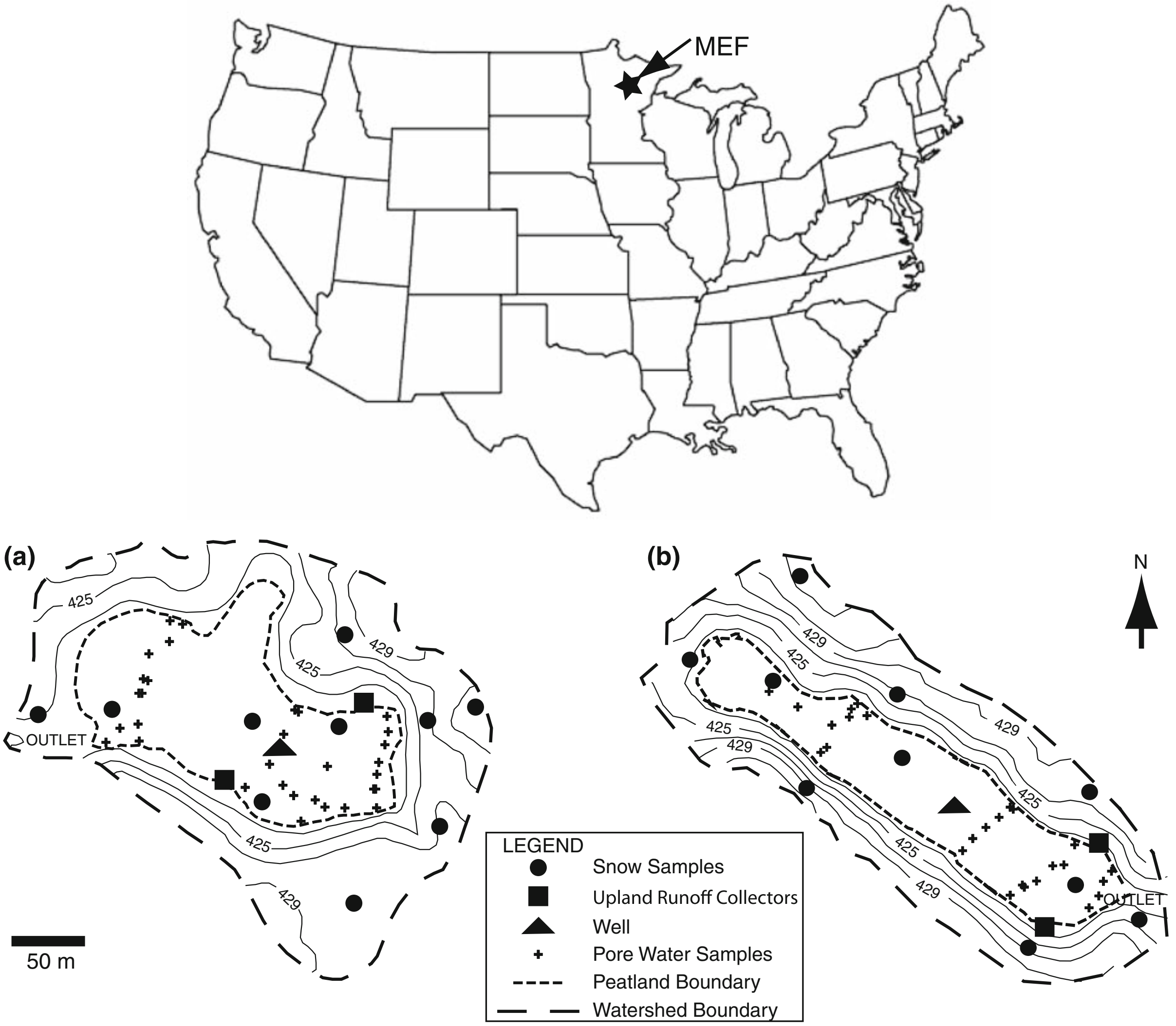

Fig. 1 Location of the study area, Marcell Experimental Forest (MEF) in north-central Minnesota and the two study watersheds S2 (**a**) and S6 (**b**)

records of wet deposition chemistry including Hg concentration are available for MEF.

Generally, the glaciated terrain of the area is typical of the western Great Lakes region and is characterized by rolling upland topography with numerous small lakes and wetlands. Peat soils were formed from *Sphagnum* mosses and herbaceous plants over limnic materials and glacial sediment, which accumulated in an ice-block depression (Verry and Timmons 1982). Deep upland soils were formed from Wisconsinan glacial drift. Above this glacial till (B-horizon), surface soil consists of a shallow, 2–7 cm organic surface horizon (O-horizon) overlying approximately 30 cm of sandy loam (A-horizon). During wet periods, interflow in the upland soil moves along the upper boundary of the low permeability B-horizon toward the peatland in each watershed (Timmons et al. 1977). Both watersheds are in headwater areas. Hydrological inputs to the upland forests are solely via precipitation. Hydrological inputs to the peatlands are via precipitation, interflow, and some surface runoff from the surrounding forested uplands, ultimately draining through a monitored watershed outlet (Fig. 1). In addition to surface runoff from the watersheds, some water is lost via deep groundwater seepage (Nichols and Verry 2001). Losses via groundwater seepage were not measured in this study.

Peatland vegetation in both watersheds is similar, consisting of *Sphagnum* mosses with an overstory of black spruce (*Picea mariana*) and tamarack (*Larix laricina*) and an understory of ericaceous shrubs such as Labrador tea (*Ledum groenlandicum*), leatherleaf (*Chamaedaphne calyculata*), and bog rosemary (*Andromeda polifolia*). Paper birch (*Betula papyrifera*) and speckled alder (*Alnus rugosa*) are found along the outer margins of each peatland. Upland vegetation in watershed S2 is composed mainly of trembling aspen (*Populus tremuloides*) and *B. papyrifera* with an understory of hazel (*Corylus*) species, ferns and herbs. The upland forest of watershed S6 was experimentally clear-cut in 1980 to convert the aspen forest to white spruce (*Picea glauca*) and red pine (*Pinus resinosa*).

Climate at MEF is characterized as sub-humid continental. January and July air temperatures were −16 and 20°C, respectively during the 2005 study year and total precipitation for 2005 was 672 mm, which are typical values for this region (Verry and Timmons 1982). During this 12-days study period (March 31–April 12, 2005), melting snow was the sole hydrological input; there were no additional precipitation inputs.

Water and snow sampling

Snow samples were collected at 10 random locations (Fig. 1) in each watershed on April 1, 2005 using an HCl acid-rinsed acrylic snow corer to obtain full depth samples and immediately placed in 4-l plastic bags pre-rinsed with 10% HCl. The samples were filtered following the melting of the snow at 20°C in the dark, acidified, and stored in Teflon bottles. Peatland pore waters were collected along several transects crossing the entire width of each peatland on April 5–6, 2005. Individual sampling locations are indicated on Fig. 1. Peat pore water samples were collected from unfrozen peat areas over an integrated depth of 2.5–7.5 cm below the peat surface using a Teflon piezometer with a 5 cm slotted end.

On upland hillslopes, pairs of surface and subsurface runoff collector plots have been monitored since 1971 by the US Forest Service (see Timmons et al. 1977; Verry and Timmons 1982). For subsurface runoff (interflow), a perforated 1.82 m stainless steel pipe, horizontally buried at the A–B horizon interface feeds into another polyvinyl chloride (PVC) pipe and empties into a polyethylene collection tank. For surface runoff, a stainless steel box extending to the bottom of the O-horizon feeds into a PVC pipe, which empties into a separate polyethylene collection tank. Runoff accumulating in collection tanks in watershed S2 was monitored using continuous float recorders. Runoff accumulating in collection tanks in watershed S6 was monitored manually at least every other day during the snowmelt period. Upland interflow samples were collected on four different dates in each watershed. In watershed S2, these dates were April 2, 4, 7, and 9, 2005. In watershed S6, upland runoff was sampled on March 31, April 4, 7, and 9, 2005. Only one upland surface runoff sample was collected in each watershed (March 31 in S6 and April 2 in S2) as upland surface runoff only occurred early in the study period. Thus, in total, nine upland runoff samples (two locations on four dates for interflow samples and one location on one date for surface samples) were collected from each watershed. When both surface and interflow runoff occurred, concentrations were flow-weighted according to the accumulation of water in the respective collection tanks.

Between March 31 and April 11, 2005, water samples were collected at least daily from outlet weirs. This sampling period encompassed the start of snowmelt discharge and most of the hydrograph recession limbs. To compare snowmelt fluxes to annual fluxes, samples were also collected for the remainder of 2005 from outlet weirs approximately bi-weekly when flowing. Watershed S2 flowed for 244 days and watershed S6 flowed for 299 days in 2005. In addition to the snowmelt period, 15 samples from the outlet of watershed S2 and 24 samples from the outlet of watershed S6 were obtained. For both watersheds, concentrations between measurement dates were estimated by linear interpolation of concentration values.

Ultra-clean trace metal protocols were used at all times for the preparation of sampling equipment and for the sampling of water in the field (Gill and Fitzgerald 1987). All samples were filtered (ashed 0.7 µm glass fiber filters). Unfiltered samples were also collected at watershed outlets, but due to the similarity in concentrations between filtered and unfiltered samples, this study concentrates solely on filtered samples. All samples were acidified to 0.5% with concentrated ultrapure HCl for THg and MeHg analysis and stored in Teflon bottles. Samples for DOC analysis were stored in HDPE bottles.

Hydrological methods

Discharge from each watershed was measured below the peatland outlets over 120° V-notch weirs using continuous recording stream gauges installed by the US Forest Service and monitored continuously since 1961. Discharge was averaged daily. Daily discharge was further separated into either peatland discharge or upland discharge using a US Forest Service hydrograph separation technique (see Timmons et al. 1977; Verry and Timmons 1982). This is a physical hydrograph separation technique specifically derived and calibrated for these two watersheds. Briefly, historical records of July and August hydrograph recessions legs under a variety of flow conditions were used to calculate an average recession leg for flow originating only from the peatland. This peatland-only source was verified through concomitant observations of no water accumulation in the upland runoff collectors. Peatland-water-only hydrographs were then constructed using the average peatland recession leg and physically measured rising legs. Upland runoff in each watershed was then estimated as the difference between the measured hydrographs and the constructed peatland-water-only hydrographs.

Peatland water table elevation was measured using a large diameter (30 cm) well equipped with a float recorder in each of the studied peatlands (see Fig. 1). Snow water equivalent (SWE) in the watershed snowpack was estimated from snow course measurements made during the 2005 snow accumulation season. Average SWE was calculated using an arithmetic mean from samples in open-upland ($n = 10$), open-peatland ($n = 10$), deciduous-upland ($n = 50$), coniferous-upland ($n = 10$), and coniferous-peatland ($n = 20$) then scaled to each watershed by multiplying by the percentage of cover type.

Calculation and source attribution of fluxes

The calculation of THg and MeHg fluxes from each watershed outlet during the snowmelt period was:

$$\text{Hg Flux} = [\text{Hg}] \times Q \qquad (1)$$

where [Hg] is the concentration of the mercury species, either THg or MeHg (ng l^{-1}); Q is the watershed discharge (l day^{-1}). Annual fluxes of THg and MeHg from each watershed were calculated by summing daily fluxes for days when there was watershed discharge. Yields were further calculated by dividing the flux by watershed area (km^2).

To estimate the individual contributions of upland and peatland runoff (the compartments) as sources of Hg in watershed export, we adopted a simple mass balance approach. To calculate fluxes attributable to upland runoff, concentrations measured in upland runoff collectors were multiplied by the volume of runoff calculated in the hydrograph separation. Fluxes attributable to peatland runoff were then calculated by subtracting upland fluxes from the total watershed fluxes measured at watershed outlets (Eq. 1). The importance of melting snow as a third end-member to THg and MeHg dynamics in these watersheds was inferred through differences in upland and peatland contributions, snowpack concentrations, SWE measurements, and the analysis of other chemical variables, specifically THg:DOC and MeHg:DOC ratios.

Since DOC is an important vector for Hg transport (Driscoll et al. 1995; Kolka et al. 1999), we investigated whether monitoring THg:DOC and MeHg:DOC ratios in different hydrological compartments and at each watershed outlet might provide a further line of evidence for our attribution of Hg sources. While previous work has not specifically monitored Hg:DOC ratios through time, other distinct metal:DOC ratios such as landcover-based groups (including wetlands) of Al:DOC ratios have been shown to be relatively constant during the spring flood in a boreal Swedish catchment (Cory et al. 2006). In our analysis therefore, we assume that changes in THg:DOC and MeHg:DOC ratios in watershed discharge are a function of changes in THg or MeHg sources. In interpreting this data we note that since both THg and MeHg concentrations are orders of magnitude less than DOC concentrations, ratios are very small. We have thus presented the ratios as logarithms.

Analytical methods

THg and MeHg analyses were performed in a Class 100 cleanroom at the University of Toronto by US Environmental Protection Agency (USEPA) Methods

1630 (USEPA 2001) and 1631 (USEPA 2002). MeHg concentration was determined by aqueous phase ethylation, trapping, column separation, pyrolysis to Hg^0, and detection by cold vapor atomic fluorescence spectroscopy (CVAFS) following distillation (Bloom 1989; Horvat et al. 1993). Recovery of a methylmercury spike was 91 ± 12% ($n = 25$), replication of duplicates was 13 ± 8% ($n = 14$), and the detection limit, calculated as three standard deviations of distillate blanks, was 0.03 ng l^{-1} ($n = 14$). THg concentration in water was determined using a Tekran model 2600 CVAFS mercury detector with automated sampler. Recovery of a total mercury spike was 96 ± 6% ($n = 11$), replication of duplicates was 1.2 ± 0.8% ($n = 12$), and the detection limit was 0.21 ng l^{-1} ($n = 22$).

DOC was analyzed on a Shimadzu TOC-5050 Total Organic Carbon Analyzer, employing high temperature (680°C) catalytic combustion at the Canada Center for Inland Waters in Burlington, Ontario.

Statistical methods

The comparison of mean values between two sample sets, such as the comparison of discharge between watersheds, was completed using unpaired *t* tests. Analysis of variance (ANOVA) was used to assess differences in mean concentrations among multiple sample sets, such as the comparison of mercury concentrations among watershed discharge, snow, peatland pore water, and upland runoff. Pair-wise comparisons of sample means were then performed using the Tukey HSD test. Comparisons were considered statistically significant at $p < 0.05$.

Results

Hydrology

Water discharged from both watersheds during the 12-days snowmelt study period comprised a significant proportion of the annual discharge (Fig. 2a). Over the study period, discharge from watershed S2 was 5.1×10^3 m^3 (30% of annual discharge of 17×10^3 m^3) and discharge from watershed S6 was 4.1×10^3 m^3 (41% of annual discharge of 9.9×10^3 m^3). Although the duration of our sampling period comprised the entire hydrograph rising limbs, peak flows, and most of the falling limbs for both watersheds, the falling limb of the S2 watershed was under-sampled with respect to our measurements in watershed S6. This was due to the longer recession of flow in watershed S2 and our objective of sampling both watersheds over the same time period. The snowmelt period therefore comprised a slightly larger proportion of the annual flux of water from watershed S2 than we have quantified here.

Peatland water tables were at their maxima in both watersheds during the spring snowmelt (Fig. 2b). In both peatlands, the water table remained within 15 cm of the surface (in the middle of the peatland) throughout the snowmelt period. The maximum water table elevation in the S2 peatland was 8.6 cm below surface (April 5) and in the S6 peatland it was 5.6 cm below surface (April 2). Both peatlands are slightly domed toward the middle. Although water tables remained below the surface in the middle of each peatland, we did observe considerable surface water along the edges of both peatlands during snowmelt.

Upland runoff was a more important source of the water exported from watershed S2 than from

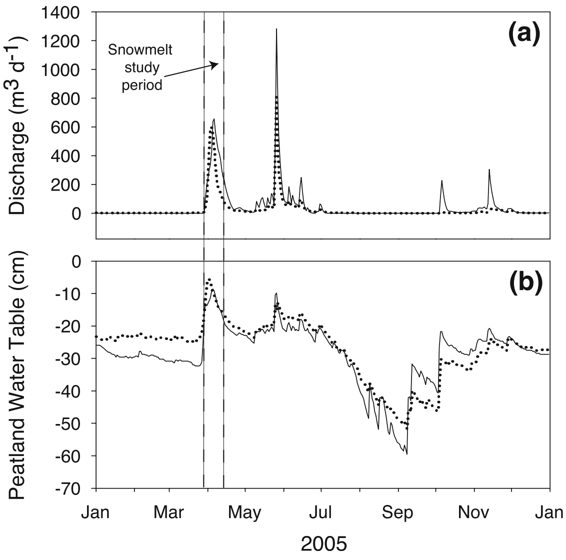

Fig. 2 Annual discharge (**a**) and peatland water table elevations (**b**) for watersheds S2 (*solid line*) and S6 (*dotted line*) in 2005. Water table elevations are with respect to the ground surface at each well. The snowmelt study period is denoted between the vertical *dashed lines*

watershed S6, but overall, peatland-derived runoff was the dominant water source in both watersheds (Fig. 3). In watershed S6, peatland-derived runoff (comprising snow melting in the peatland and water stored in peatland pore water) contributed 83% of the watershed flow. Contributions from upland-derived runoff (comprising snow melting in the upland and mobilized upland soil water) were relatively low and steady, totaling 17% of watershed runoff during the study period. In watershed S2, the contribution of upland runoff increased steadily throughout the snowmelt hydrograph, from 8% at the start of the study to 66% by the final day of sampling. The total upland contribution to the discharge from watershed S2 was 37% over the study period; considerably more than that observed for watershed S6. Although upland runoff contributed more flow in watershed S2 than in watershed S6, upland SWE in the S6 watershed was actually slightly higher than in S2. Otherwise, the SWE in watersheds S2 and S6 at maximum measured snowpack (March 18, 2005) were similar in both watersheds (Table 1). We do not have measurements of either evaporation or groundwater seepage during this period, however, our observations imply that groundwater seepage in the uplands may have been a more important loss of water from watershed S6 than from watershed S2.

In these hydrograph separations, the temporal pattern of upland runoff represents when that runoff was expressed at each watershed outlet. We are able to make rough estimates of lag times between when water ran off upland slopes and when it was observed at the outlet of each watershed (i.e., its lag time in the central peatland of each watershed) by comparing when peak flow occurred from the upland runoff collectors and when the peak contribution of upland runoff was observed in Fig. 3. In watershed S2, the greatest volume of water collected in the upland runoff collectors was observed on April 6, whereas the peak upland runoff contribution observed in the hydrograph separation was on April 10. In watershed S6, peak upland runoff was collected on April 5, whereas the peak contribution of upland runoff was observed in the hydrograph separation on April 7. Thus, lag times for upland runoff from watersheds S2 and S6 were approximately 4 and 2 days, respectively. Upland runoff therefore likely mixed with peatland waters (surface or subsurface) for between 2 and 4 days before being discharged from the watershed.

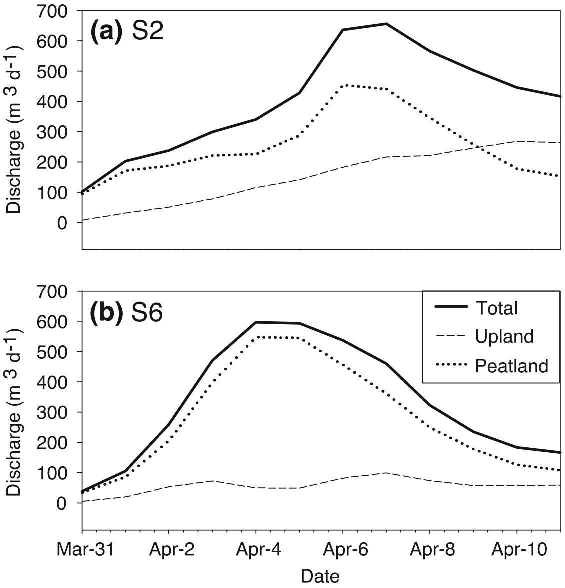

Fig. 3 Hydrograph separations of discharge in watersheds S2 (**a**) and S6 (**b**), partitioning total discharge between upland runoff and peatland runoff sources

Table 1 Snow water equivalent (SWE) at peak snowpack and associated discharge during the snowmelt period for peatland, upland, and total watershed components

	S2			S6		
	Peatland	Upland	Total	Peatland	Upland	Total
SWE	3.1	6.9	10	2.5	7.4	9.9
Discharge	3.0	1.8	4.8	3.3	0.68	4.0
Difference	0.11	5.1	5.1	−0.8	6.7	5.8

All values in 10^3 m^3

Water chemistry

Temporal trends in watershed discharge chemistry throughout the snowmelt hydrographs were relatively similar between watersheds S2 and S6 (Fig. 4). Despite the temporal variation in both watershed discharge and water table elevation throughout the snowmelt period, concentrations of THg in watershed discharge were relatively steady (Fig. 4; Table 2). MeHg concentrations showed no increasing or decreasing trend throughout most of the snowmelt period in watershed S2, but did start to rise near the end of our sampling campaign. In watershed S6, MeHg concentrations continually increased throughout the hydrograph. MeHg concentrations in discharge from both watersheds were inversely

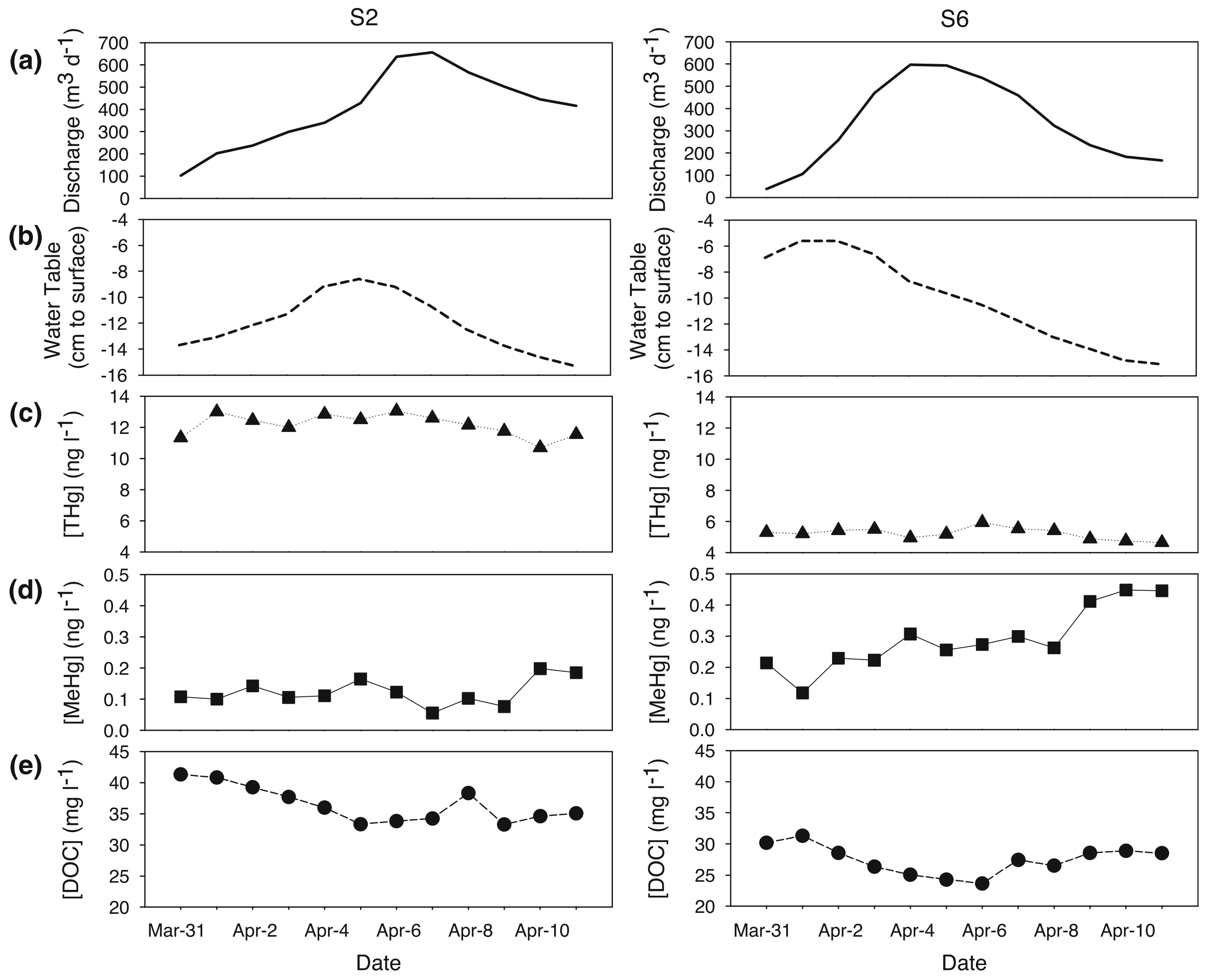

Fig. 4 Watershed discharge (**a**), water table position (**b**); total mercury concentration (THg; **c**), methylmercury concentration (MeHg; **d**), and dissolved organic carbon concentration (DOC; **e**) of watershed discharge in watersheds S2 (*left*) and S6 (*right*)

related to peatland water table position (Fig. 5). MeHg concentrations in watershed discharge were generally greater when water tables were deeper in each peatland. This relationship was significant in watershed S6, but not in watershed S2. The relationship in watershed S2 was skewed by elevated MeHg concentrations at the maximum water table elevations during snowmelt (indicated on Fig. 5). Removal of these three points resulted in a significant linear trend in watershed S2, but also suggests that pore water concentrations did not change linearly with depth in peatland S2. We are unsure if these same trends continue throughout the year. DOC concentrations showed an inverse linear relationship with snowmelt discharge (Fig. 4). The r^2 value for the relationship between DOC concentration and discharge in watershed S2 was 0.70 ($p < 0.01$) whereas in watershed S6, it was 0.83 ($p < 0.01$).

Although the temporal patterns were similar, the magnitude of concentrations differed significantly between the two watersheds. S2 had significantly higher mean concentrations of THg ($p < 0.001$) and DOC ($p < 0.001$), and significantly lower mean concentrations of MeHg ($p < 0.001$) in watershed discharge compared to S6 (Table 2). The differences in THg and MeHg concentrations between watersheds persisted during the rest of our sampling, post-snowmelt. The mean ± standard deviation of discharge samples taken post-snowmelt in S2 for THg and MeHg were 12.3 ± 3.6 ng l^{-1} and 0.36 ± 0.31 ng l^{-1}, respectively ($n = 15$). Compared to snowmelt samples from watershed S2,

Table 2 Concentrations of total mercury (THg), methylmercury (MeHg), and dissolved organic carbon (DOC) in various hydrological compartments of watersheds S2 and S6

	Watershed S2			Watershed S6		
	[THg] (ng l^{-1})	[MeHg] (ng l^{-1})	[DOC] (mg l^{-1})	[THg] (ng l^{-1})	[MeHg] (ng l^{-1})	[DOC] (mg l^{-1})
Watershed discharge	12.2 ± 0.7 ($n = 15$)	0.12 ± 0.05 ($n = 15$)	36.0 ± 2.8 ($n = 15$)	5.3 ± 0.4 ($n = 15$)	0.28 ± 0.10 ($n = 15$)	27.3 ± 2.2 ($n = 15$)
Snow	0.8 ± 0.2 ($n = 10$)	0.07 ± 0.03 ($n = 10$)	All < d.l.[a] ($n = 10$)	0.8 ± 0.2 ($n = 10$)	0.05 ± 0.01 ($n = 10$)	0.5 ± 0.4 ($n = 10$)
Upland runoff	13.5 ± 4.8 ($n = 9$)	0.08 ± 0.05 ($n = 9$)	18.7 ± 2.5 ($n = 9$)	12.5 ± 3.9 ($n = 9$)	0.08 ± 0.03 ($n = 9$)	24.6 ± 19.4 ($n = 9$)
Peatland pore water	7.8 ± 1.7 ($n = 32$)	0.19 ± 0.37 ($n = 32$)	27.9 ± 8.4 ($n = 32$)	6.2 ± 1.8 ($n = 26$)	0.89 ± 1.3 ($n = 26$)	24.5 ± 4.8 ($n = 26$)

Values are mean ± standard deviation

[a] Less than detection limit

post-snowmelt discharge samples had significantly higher MeHg concentrations ($p = 0.012$), but THg concentrations were not significantly different. In watershed S6, THg and MeHg concentrations in discharge, post-snowmelt, were 7.0 ± 2.8 ng l^{-1} and 1.0 ± 0.57 ng l^{-1}, respectively ($n = 24$). Compared to snowmelt samples, post-snowmelt samples had significantly greater concentrations of both THg ($p = 0.008$) and MeHg ($p < 0.001$).

During the snowmelt period, MeHg and THg concentrations also varied considerably among snow, upland runoff, and peatland pore water in the two study watersheds (Table 2). THg concentrations were greatest in upland runoff in both watersheds and lowest in snow. MeHg concentrations were greatest in the peatland pore waters and least in snow. MeHg concentrations in upland runoff were slightly higher than those observed in snow, but only significantly so in watershed S6 ($p = 0.003$). In both the snowpack and upland runoff, MeHg concentrations were not significantly different between watersheds. Substantial variability was observed in pore water MeHg concentrations within each peatland (Table 2). MeHg concentrations in pore waters were significantly higher in peatland S6 than in peatland S2 ($p = 0.005$). Disproportionately high MeHg concentrations were found in the S6 peatland, at the interface between peatland and upland, with a maximum MeHg concentration of 6.2 ng l^{-1}.

As a supplementary means of attributing changes in watershed discharge chemistry to possible changes in hydrologic source, we analyzed THg:DOC and MeHg:DOC ratios in discharge, snow, upland runoff, and peatland pore water. To ascribe the changes in chemistry to changes in the magnitude of hydrologic sources over time, THg:DOC and MeHg:DOC ratios must differ between the possible contributing hydrologic compartments. In watershed S2, THg:DOC ratios were significantly greater in upland runoff than in peatland pore water or discharge ($p < 0.001$), but differences in MeHg:DOC ratios were not significant among compartments (Fig. 6a). In watershed S2, ratios in snow could not be examined because DOC concentrations were below the detection limit in all snow samples from this watershed. In watershed S6, THg:DOC ratios were not significantly different between discharge and peatland pore water, but ratios were significantly different in all other comparative iterations (all $p < 0.01$), and noticeably

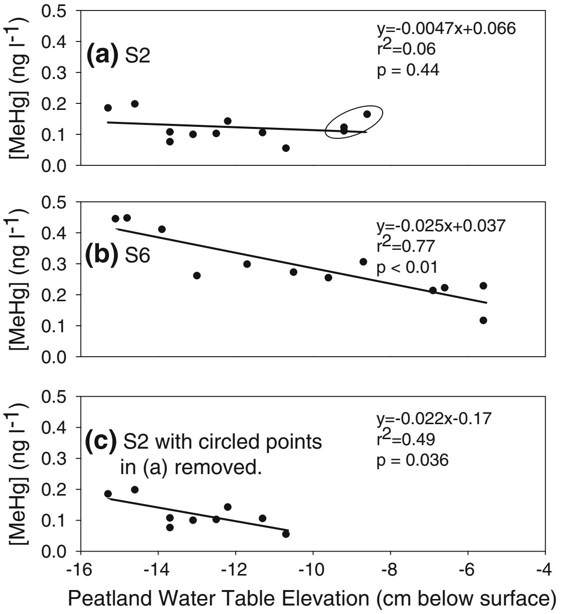

Fig. 5 Relationships between MeHg concentration in watershed discharge and peatland water table elevation in **a** watershed S2; **b** watershed S6; **c** watershed S2 with data points circled in (**a**) removed

higher in snow. Neither peatland pore water nor upland runoff MeHg:DOC ratios were significantly different from the watershed S6 discharge ratio, but peatland pore water and upland runoff MeHg:DOC ratios were significantly different from one another ($p < 0.01$). MeHg:DOC ratios in snow of watershed S6 were significantly greater than ratios in all other measured compartments ($p < 0.001$). Thus overall, THg:DOC ratios were different enough to ascribe differences in hydrologic source in both watersheds, apart from the role of melting snow in watershed S2. MeHg:DOC ratios were different enough only in watershed S6 to ascribe differences in hydrologic source.

Mercury fluxes and sources

Due to the relatively stable concentration of THg throughout the snowmelt hydrographs of both watersheds, the daily flux of THg from each watershed was closely associated with discharge. Approximately 26% and 39% of the annual THg flux from watersheds S2 and S6, respectively, occurred during the 12-days snowmelt period examined here (Table 3). The snowmelt period also accounted for 22% and 23% of the annual MeHg flux from watersheds S2 and S6, respectively. The proportion of the annual THg flux from these watersheds during the snowmelt study period was similar to the proportion of water flux, whereas the proportion of the MeHg flux was considerably less than the proportion of water flux.

Our analysis indicated that both upland runoff and peatland runoff were important sources of THg export from both watersheds, but that peatland runoff dominated as the source of MeHg (Table 3). According to our mass balance calculations, approximately 60% of the THg exported from both watersheds was from peatland runoff, with the remaining 40% from upland runoff. Upland runoff was a minor component for MeHg fluxes from the watersheds. Our estimates indicate that 21% of the MeHg exported from watershed S2 was derived from upland runoff. From watershed S6, we estimate that only 5% of the MeHg exported was derived from upland runoff.

In attempting to partition watershed Hg fluxes between peatland and upland sources, we combined the simple mass balance approach above with measurements of THg:DOC and MeHg:DOC ratios in various hydrologic compartments and watershed discharge. The THg:DOC and MeHg:DOC ratios in watershed discharge varied temporally, possibly in response to changes in the source of hydrologic flux (Fig. 6b). THg:DOC ratios peaked in both watersheds at or shortly after peak flow, with ratios remaining more elevated in watershed S2 compared to the decrease observed in S6. Also, THg:DOC ratios in S2 were higher than those in S6. The temporal variability in MeHg:DOC ratios was greater than that observed for THg:DOC ratios. MeHg:DOC increased throughout the hydrograph of both watersheds, apart from a dip in watershed S2 following peak flow.

Discussion

Importance of spring snowmelt to mercury export

The amount and timing of discharge during the snowmelt of 2005 were within the range of historical observations at the MEF. Mean ± standard deviation of April discharge from watersheds S2 and S6 between 1964 and 2005 were $4.7 \times 10^3 \pm 2.7 \times 10^3$ m^3 and $5.3 \times 10^3 \pm 3.5 \times 10^3$ m^3, respectively (US Forest Service, unpublished data). April discharge from the

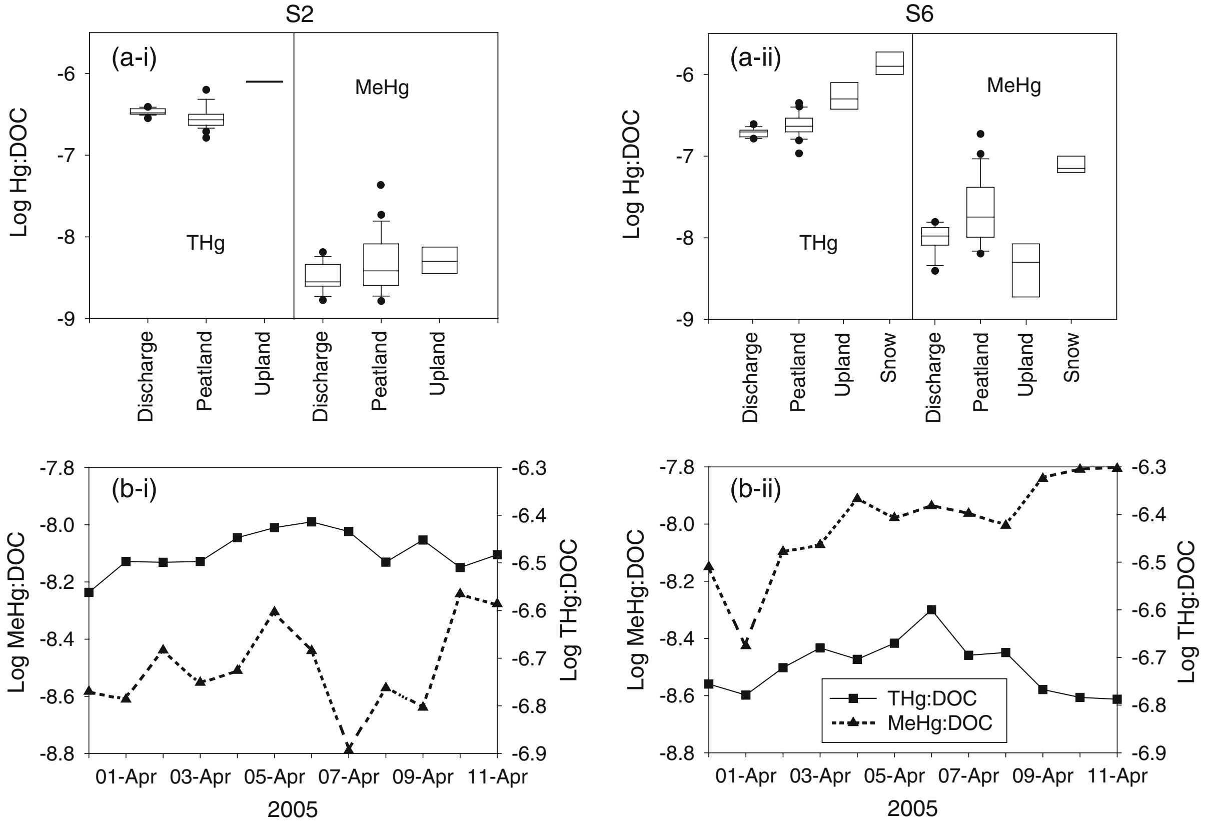

Fig. 6 Top: Log Hg:DOC ratios in various hydrological compartments in each of watersheds S2 (**a-i**) and S6 (**a-ii**). Ratios in snow for watershed S2 were not calculated because DOC concentrations were below detection limit. Bottom: Time series of log Hg:DOC ratios during the snowmelt period in watersheds S2 (**b-i**) and S6 (**b-ii**).

Table 3 Upland, peatland, and total watershed fluxes of total mercury (THg) and methylmercury (MeHg) during the studied snowmelt period compared to total watershed annual fluxes

	Watershed S2		Watershed S6	
	THg flux (mg)	MeHg flux (mg)	THg flux (mg)	MeHg flux (mg)
Snowmelt upland runoff flux	24	0.14	8.5	0.054
Snowmelt peatland runoff flux	35	0.52	13	1.0
Total snowmelt watershed flux	59	0.66	21	1.1
2005 annual	230	3.0	54	4.7

study year here in watersheds S2 and S6 was 6.3×10^3 m^3 and 4.7×10^3 m^3, respectively; both within one standard deviation of the historical mean and of a similar magnitude to one another. The snowmelt of 2005 therefore did not represent a year of abnormally high or low spring runoff and thus can be considered representative of general snowmelt conditions in these watersheds. Despite the study period corresponding to only 3.3% of the year, the importance of the spring snowmelt period to mercury fluxes from upland–peatland watersheds must be stressed because this period was disproportionately important to annual THg and MeHg fluxes.

Total mercury

THg and MeHg yields in watersheds S2 and S6 were generally within or at the high end of yields from other wetland-dominated watershed studies under high-flow conditions (Table 4). For comparison, yields in Babiarz et al. (1998) were separated by month. We compare our yields to yields they denoted as "high-flow events"; these included months with large rainstorms in addition to snowmelt. Yields in Loseto et al. (2004) were calculated over the duration of the snowmelt study period as were ours. Yields in Schuster et al. (2008) represent the range of instantaneous daily yields from several different watersheds, all with relatively sparse wetland cover. The yield of THg from watershed S2 was at the high end of the range presented here, but this is largely a concentration-driven discrepancy. Our previous research has suggested that the S2 peatland is under more oxic conditions than the S6 peatland, leading to higher levels of aerobic decomposition and Hg dissolution (Mitchell et al. 2008). Previous research also indicated that peatland pore water THg concentrations in S2 were much greater than concentrations in S6 during the growing season (Mitchell et al. 2008). Thus, the high yield of THg from watershed S2 in this study may be due to the larger pool of THg in the S2 peatland and/or differences in hydrological flow paths transporting Hg from these watersheds. Our results did indicate that a higher proportion of upland runoff in S2 was observed at the watershed outlet (Table 1) and that upland runoff concentrations of THg were elevated (Table 2).

The proportions of THg exported from both watersheds during the snowmelt study period were very similar to the proportions of water flux during this period. This, in addition to the invariant concentrations of THg throughout the hydrographs, suggests a direct hydrological control on THg flux from these watersheds. Because MeHg is the Hg species that accumulates in aquatic biota, the importance of MeHg flux during this time period is the central concern. Still, the large, short-term flux of THg from these watersheds during snowmelt may also be biologically important for mercury methylation in downstream water bodies, soils, or sediment.

Methylmercury

MeHg yields from both watersheds during the snowmelt period fall within the ranges observed by Babiarz et al. (1998) in boreal/temperate wetland-dominated watersheds and Schuster et al. (2008) in several watersheds of Sleepers River in Vermont under high-flow conditions, but are considerably larger than those observed by Loseto et al. (2004) in the High Arctic during snowmelt (Table 4). The wetland studied by Loseto et al. (2004) was a shallow deposit of peat relative to this study or Babiarz et al. (1998). Wetland coverage in the Schuster et al. (2008) study was considerably less than our study and indicated that riparian zone or stream channel methylation may have been the main driver for MeHg production there. The compared wetland watersheds were also situated in very different climates. All of these factors, but most likely the differences in climate, contributed to the discrepancy in findings among these studies.

Table 4 High-flow yields of total mercury (THg) and methylmercury (MeHg) from this and other studies in watersheds containing wetlands

High-flow yield			
THg yield (mg km^{-2} day^{-1})	MeHg yield (mg km^{-2} day^{-1})	% watershed as wetland	Reference
3.6–16	0.23–1.6	5–45	Babiarz et al. (1998)[a]
27–38	0.0008–0.002	Unknown[b]	Loseto et al. (2004)
~0–150[c]	0.54–2.3[d]	1–5	Schuster et al. (2008)
53	0.60	32	This study—watershed S2[e]
20	0.99	27	This study—watershed S6[e]

[a] Calculated on a monthly basis only for watersheds with wetlands; includes flow due to large rainstorms in addition to snowmelt

[b] Percentage cover of wetlands in this study is not indicated; samples were collected directly from wetland runoff

[c] Range of THg fluxes from six different watersheds on a daily instantaneous basis

[d] Approximate mean particulate MeHg yields from two watersheds (W-5 and W-9BX) during snowmelt

[e] Yields calculated only from data over study time period (12 days). Annual yields (per day) were considerably less

Although it is still an important period of time for MeHg transport to downstream aquatic ecosystems, the proportional export of MeHg from each of our study watersheds during the snowmelt period was considerably less than the proportional flux of water over the same time period. In other words, the concentration of MeHg in water discharged from these watersheds was considerably less than that observed later in the year. Since the production of MeHg is a microbially mediated reaction linked to the activity of sulfate-reducing bacteria (Gilmour et al. 1992), mercury methylation may have been suppressed and MeHg demethylation possibly enhanced due to cold temperatures (Bodaly et al. 1993). For comparison, median MeHg concentrations of peatland pore water during the study period in S2 (0.10 ng l^{-1}) were less than observed between June and October (0.37 ng l^{-1}; Mitchell et al. 2008). Thus, discharge of low MeHg concentration meltwater and/or the flushing of areas of low net MeHg production and/or small pools of MeHg within the S2 watershed resulted in low MeHg concentrations in discharge. It appears, however, that the slightly elevated MeHg concentrations observed at the highest water table elevations in S2 (Fig. 5a) may have been important to the MeHg that was discharged from this watershed. It is possible that zones of higher MeHg production and/or accumulation exist closer to the peat surface in S2, however any MeHg produced there is rarely flushed out since water tables are infrequently at this level.

In contrast to observations in watershed S2, MeHg concentrations in peatland pore waters remained elevated in watershed S6 during the spring snowmelt (median = 0.37 ng l^{-1}), at a similar level to that observed throughout the rest of the year (median = 0.35 ng l^{-1}; Mitchell et al. 2008). Our sampling strategy does not allow us to discern whether active mercury methylation was taking place during snowmelt or whether the MeHg observed in pore water was due to its preservation and storage from earlier periods. However, if we estimate the active pore water MeHg pool by multiplying the area of the peatland (2.4 ha) by a 0.1 m drop in water table over the snowmelt period, multiply this by a mean porosity for surface peat in S6 of 0.89 (unpublished data), and finally by the median concentration of MeHg in pore water, the pore water pool of MeHg in 10 cm of peat at S6 was approximately 0.79 mg. This is slightly less than the 1.1 mg of MeHg that was discharged from S6 during the snowmelt period (Table 4), suggesting either that some active methylation was occurring during snowmelt or that other sources, such as melting snow or upland runoff, contributed some of the MeHg. We note also that considerable spatial variability in peatland pore water concentrations was observed, with several high concentration outliers, especially at the upland–peatland interface. Another possible explanation is thus that high MeHg concentrations sources near the outer edges of the peatland contributed more to outflow, as has been suggested by previous research at the MEF (Urban et al. 1989; Mitchell et al. 2008). Finally, the linear trend between water table elevations and MeHg concentrations in discharge (Fig. 5b), in relation to the increasing trend in MeHg concentrations in discharge, suggests that peatland pore water drainage was important to MeHg export from watershed S6. We expand on the differences in hydrologic sources and subsequently, in MeHg and THg discharge from both watersheds, in the following section.

Sources of total mercury and methylmercury during snowmelt

In both our mass balance and mercury-to-DOC ratio approaches we assumed that THg and MeHg in upland runoff and melting snow were conserved while transported to the watershed outlet. We provide here the caveat that this assumption is difficult to confirm because there likely was mixing between upland runoff, snow, and peatland waters prior to export from the watershed outlet. We know that upland runoff likely mixed with peatland pore waters and/or surface water stored on the peatland for 2–4 days prior to being exported from each watershed, however, we have no information on how this lag time affects the upland runoff chemistry. This is one reason why we have set about this problem with multiple approaches. Little quantitative information exists on the temporal stability of Hg complexes as they are transported through watersheds such as those studied here. This presents an important avenue of future research, but we contend that the only present means of attaining such information would be through tracer studies involving additions of enriched stable Hg isotopes (i.e., Harris et al. 2007). In lieu of having this information, it remains likely that any change in upland runoff or snow chemistry is due to interactions within the peatland pore waters and not because waters have bypassed this interaction via other hydrologic pathways (i.e., surface flow). We thus contend that our estimates of the importance of the peatland itself as a source of mercury, using these approaches, should be conservative.

Since both THg and MeHg concentrations in snow and upland runoff were similar in both watersheds, we inferred that differences in hydrological flow paths during the snowmelt period and Hg pools were responsible for differences in Hg flux between the two watersheds. Whereas our simple mass balance indicated that THg export was similarly ascribed to upland and peatland sources, peatland runoff was the major source of MeHg to watershed export (Table 3). Other research has suggested that melting snow itself is an important source of MeHg to watershed export (Bishop et al. 1995; Loseto et al. 2004). Our model did not separate the direct role of melting snow as a third end-member source of THg or MeHg from these watersheds, but we hoped to infer the role of Hg in melting snow via comparison of upland and peatland sources and through the analysis of other chemical variables. Since upland and peatland sources of THg were similar in magnitude, it is difficult from our hydrological data alone to discern the role of melting snow as a possible third member. Thus, THg derived directly from melting snow may be important to THg in watershed export, but we are unable to quantify this source.

Conversely, there were large differences both in the flux of MeHg ascribed to each source and in the concentration of MeHg observed in different hydrologic compartments, with peatland pore waters being the source most closely associated with what was observed at the watershed outlet. If MeHg derived directly from melting snow in either the upland or peatland were significant, one would not expect to observe a large difference in MeHg concentration between upland and peatland runoff. We found that both concentrations and fluxes of MeHg from each peatland were much greater than from the uplands. This comparison strongly suggests that MeHg from melting snow in each watershed is of little significance to watershed exports. It is well established that peatlands are important sources of MeHg to downstream aquatic ecosystems during the growing season (Branfireun et al. 1996, 2005), but we confirm here that MeHg derived from peatland pore water remains an important source in similar peatland-dominated watersheds during spring snowmelt, even when the majority of the peatland surface is frozen or thawing.

In watershed S2, upland runoff was proportionately more important over time for overall watershed hydrological export. In comparison, upland runoff in watershed S6 was relatively steady throughout the sampling period and its volume was considerably less than that observed in watershed S2 (Fig. 3). These observations would suggest that Hg dynamics observed at the watershed outlet in watershed S2 would reflect the increasing importance of upland runoff whereas in watershed S6, the proportioning of flow between peatland pore water and snow meltwater should more strongly control chemistry at the watershed outlet. Unfortunately, Hg:DOC ratios in watershed S2 were not particularly useful in providing further evidence for these observations because few significant differences existed between measured compartments and snow was not quantifiable due to very low DOC concentrations (Fig. 6). In watershed S6, there were large differences in THg:DOC ratios between compartments. The THg:DOC ratio signature in watershed discharge was not significantly different from the signature in peatland pore waters. This lack of difference further supports the importance of peatland pore waters as a source of THg. The peak in the THg:DOC ratio following peak discharge may be due to dilution of the peatland pore water signal by snow melting within the peatland. A larger role for melting snow may have been important here, but the dissimilarity of its THg:DOC ratio to that observed in watershed discharge suggests that it is far from the dominant source. In all, this THg:DOC data supports our prior observations that both peatland runoff and upland runoff were important sources of THg in watershed export, with peatland runoff being the more important of the two.

With respect to MeHg:DOC ratios, watershed discharge and peatland pore water ratios were not significantly different in watershed S6, supporting our observations that peatland pore waters dominate as a source of MeHg. It would appear that initially low MeHg:DOC ratios in watershed discharge must have been the result of more upland runoff. Ratios fell off thereafter, possibly reflecting a dual source between peatland pore waters and snow, but our observations more strongly reflect the role of peatland pore water drainage and its relation to elevated MeHg concentrations (Fig. 5).

The relatively minor role of MeHg derived from melting snow in these watersheds contrasts with other wetland Hg research under snowmelt conditions (Bishop et al. 1995; Loseto et al. 2004), which suggests that snow-derived MeHg is a dominant part of the overall mass balance. By looking only at MeHg pools, there was approximately 0.7 mg of MeHg in snow at maximum snowpack in all of watershed S2 and 0.5 mg of MeHg in snow in watershed S6. These pools are approximately equal to the quantity of MeHg discharged from watershed S2 during snowmelt, but less than half that observed from watershed S6. Certainly some of this pool was lost to deep seepage in the uplands, to longer-term storage within the watersheds, and possibly to demethylation. Thus, although a significant pool of MeHg may be stored in snow, our study suggests that melting snow does not contribute as much to watershed discharge of MeHg as does peatland pore water drainage. The contrast between our study and previous research may be attributed to geographic, climatic and geomorphic factors, but we also suggest that the importance of MeHg or THg from within-basin, non-snowpack sources is simply not observable when a whole-basin input–output approach is taken.

Conclusions

Although the melting of snow in the spring is a relatively short and cold time of year, it is disproportionately important to the annual fluxes of THg and MeHg from peatland-dominated watersheds in the Great Lakes northern temperate region. This 12-days snowmelt study period comprised between 26% and 39% of annual THg export and between 22% and 23% of annual MeHg export. The proportional THg export during snowmelt was similar to the proportional export of water, but the proportional MeHg export was less, likely due to increased net production of MeHg later in the year when temperatures are warmer and microbial communities are more active.

Previous research has not gone far enough to adequately link hydrological fluxes from wetland-dominated watersheds to the overall export of harmful contaminants such as mercury. This is the first study of its kind to comprehensively attribute total watershed export of MeHg and THg to particular source areas. Monitoring THg:DOC and MeHg:DOC ratios proved to be a valuable tool in addition to hydrological monitoring and our simple mass balance for apportioning Hg in watershed export to specific sources. Melting snow in northern temperate peatland-dominated watersheds is responsible for only small amounts of MeHg export during snowmelt. We were unable to accurately estimate the direct role of melting snow on THg export, but it appears to be more important than is melting snow for MeHg export. The principal importance of melting snow is hydrological, controlling the initiation of upland runoff, the mobilization of THg in upland soils, and the mobilization of MeHg in peatland pore waters. Upland runoff and peatland runoff were generally equally important and dominant as sources of THg to watershed export during snowmelt. In contrast to previous research where meltwater dominates, peatland pore waters were by far the dominant source of MeHg to watershed export during the spring snowmelt period.

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