

Mercury dynamics in relation to dissolved organic carbon concentration and quality during high flow events in three northeastern U.S. streams

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[1] Mercury (Hg) contamination is widespread in remote areas of the northeastern United States. Forested uplands have accumulated a large reservoir of Hg in soil from decades of elevated anthropogenic deposition that can be released episodically to stream water during high flows. The objective of this study was to evaluate spatial and temporal variations in stream water Hg species and organic matter fractions over a range of hydrologic conditions in three forested upland watersheds (United States). Mercury and organic matter concentrations increased with discharge at all three sites; however, the partitioning of Hg fractions (dissolved versus particulate) differed among sites and seasons. Associated with increased discharge, flow paths shifted from mineral soil under base flow to upper soil horizons. As flow paths shifted, greater concentrations of dissolved organic carbon (DOC) richer in aromatic substances were flushed from upper soil horizons to stream water. The hydrophobic organic matter associated with humic material from upper soils appears to have had a greater capacity to bind Hg. Because of the strong correlation between Hg and DOC, we hypothesize that there was a concurrent shift in the source of Hg with DOC from lower mineral soil to upper soil horizons. Our study suggests that stream discharge is an effective predictor of dissolved total Hg flux.

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1. Introduction

[2] Mercury (Hg) is a potent neurotoxin that poses a risk to the health of both humans and wildlife [Wiener *et al.*, 2003]. Concentrations of Hg in excess of human and wildlife health criteria have been observed in biota throughout the northeastern United States and southeastern Canada [Evers *et al.*, 2007; Driscoll *et al.*, 2007]. Methylmercury (MeHg) is efficiently bioaccumulated in the aquatic food chain and humans are primarily exposed to MeHg through the consumption of fish. All 50 states in the United States have fish consumption advisories for some or all water bodies to limit Hg exposure.

[3] The majority of Hg that accumulates in biota originates from anthropogenic activities (e.g., combustion of fossil fuels, industrial processes, incinerators) that release Hg to the atmosphere. Anthropogenic sources of Hg have exceeded natural inputs since the beginning of the industrial

revolution [Fitzgerald *et al.*, 1998]. Globally, atmospheric Hg deposition is approximately three times greater than preanthropogenic levels [Mason *et al.*, 1994], with some regions showing a considerable increase beyond these levels [Lorey and Driscoll, 1999]. Long range transport of atmospheric Hg has caused widespread contamination in relatively pristine areas, including the northeastern United States. The sediment and soils of forested watersheds in the northeastern United States and Canada contain large pools of legacy Hg from historical deposition [Mason *et al.*, 1994; Lorey and Driscoll, 1999; Harris *et al.*, 2007].

[4] The Hg accumulating in forest soil and sediments is a mix of “new Hg” and “old Hg.” New Hg is defined as recently deposited Hg from natural and anthropogenic sources, whereas older legacy Hg represents historical deposition [St. Louis *et al.*, 2001; Hintelmann *et al.*, 2002; Demers *et al.*, 2007]. Newly deposited Hg is likely more reactive and more readily transformed to MeHg and, therefore, is potentially more available for assimilation by biota than older legacy Hg [Orihel *et al.*, 2006; Harris *et al.*, 2007].

[5] Mercury deposition has declined over the past few decades [Pirrone *et al.*, 1998; Lorey and Driscoll, 1999; Schuster *et al.*, 2002; Bookman *et al.*, 2008; Butler *et al.*, 2008] due to controls on medical waste incinerators and municipal waste combustors (see Mercury Study Report to Congress 1997; <http://www.epa.gov/ttn/atw/112nmerc/volume2.pdf>). Additional controls on Hg emissions from

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electric utilities are also planned within the next decade (<http://www.epa.gov/mercuryrule/>). A critical question associated with proposed controls on Hg emissions from electric utilities and other sources is to what extent and how quickly will ecosystems respond to decreases in atmospheric Hg deposition? The answer to this question depends, in large part, on the fate of the large pool of Hg stored in vegetation and soils of the upland landscape [Krabbenhoft *et al.*, 2004].

[6] The transport of Hg through a watershed is closely coupled with the movement of both dissolved and particulate organic matter (OM) [Driscoll *et al.*, 1994, 1995; Schuster *et al.*, 2008; Shanley *et al.*, 2008]. Ionic Hg (Hg II) strongly binds with reduced sulfur sites within natural OM [Skylberg *et al.*, 2000; Haitzer *et al.*, 2003]. The Hg retained in soils can be released episodically to stream water during high flows when near-stream saturated areas connect terrestrial organic soils with the stream. Elevated fluxes of Hg and OM have been observed during high flow events from upland forested watersheds across the northeast [Schuster *et al.*, 2008; Shanley *et al.*, 2008; Demers *et al.*, 2010]. High flow periods during spring snowmelt or summer storms can represent a large portion of the annual water and chemical flux from a watershed [Babiarz *et al.*, 1998; Scherbatskoy *et al.*, 1998; Shanley *et al.*, 2008]. In some instances, a single high flow event can contribute a large fraction (up to 50%) of the annual Hg export from a watershed [Babiarz *et al.*, 1998; Scherbatskoy *et al.*, 1998]. Uplands, therefore, can be an important source of Hg (II) for downstream zones of methylation (i.e., wetlands, lakes).

[7] The drainage waters of upland forested watersheds can also act as a source of MeHg to downstream aquatic ecosystems where it is available for biological uptake [Schuster *et al.*, 2008; Shanley *et al.*, 2008]. Net methylation of Hg (II) primarily occurs in reducing zones such as lake sediments and wetlands; however, methylation also occurs in the riparian areas and near-stream zones of upland watersheds [Bishop *et al.*, 1995; Driscoll *et al.*, 1998]. The production and transport of MeHg is driven by seasonal changes in conditions of watershed saturation, temperature, microbial activity, and discharge [Selvendiran *et al.*, 2008a]. Surface water MeHg concentrations are typically greatest during warmer months when biological activity, SO_4^{2-} reduction, and hydrologic residence time are greatest [Babiarz *et al.*, 1998; Selvendiran *et al.*, 2008a].

[8] It is well established that large quantities of solutes, including dissolved organic carbon (DOC), are flushed from the soil profile during precipitation and snowmelt events [Boyer *et al.*, 1997]. Under base flow conditions, surface water largely originates from groundwater primarily draining the lower mineral soil and deeper surficial deposits. As flow increases during episodic events, the flowpaths of the water shift upward to organic soil horizons [Chen *et al.*, 1984]. Recently, it has been documented that higher water tables and expanding saturated areas tend to mobilize the more reactive phases of DOC known to complex and transport Hg [Schuster *et al.*, 2008; Shanley *et al.*, 2008]. Short-term and seasonal variations in OM composition therefore can arise from shifts in flow paths, while long-term variation may result from changes in carbon (C) stocks related to climate, land use change, and changes in acidic deposition [McKnight *et al.*, 2003; Inamdar and Mitchell, 2004; Monteith *et al.*, 2007]. An understanding of tempo-

ral and spatial variability in transport mechanisms responsible for controlling the retention, transformation, and transport of Hg in forested ecosystems is essential to predicting how ecosystems will respond to changes in Hg emissions.

[9] We applied the small watershed approach at three sites in the northeastern United States to investigate stream water Hg dynamics in relation to DOC concentration and quality over a range of hydrochemical conditions. The small watershed approach allows for relatively precise estimates of chemical inputs and outputs [Likens and Bormann, 1995; Johnson *et al.*, 2000]. Stream water integrates various biogeochemical processes occurring in the small watershed [Johnson *et al.*, 2000].

[10] Earlier findings from this study suggested that in stream water there is a strong correlation between the filtered (dissolved) fraction of total Hg (THg) and the hydrophobic organic acid fraction (HPOA) of DOC and, furthermore, that UV absorbance of the DOC is an effective proxy for both HPOA and dissolved THg concentrations [Dittman *et al.*, 2009]. In this study, we expand on our earlier findings by examining Hg species and fractions (i.e., dissolved, particulate) in relation to organic matter dynamics. The objectives of this study were to (1) investigate seasonal differences in Hg and DOC dynamics during high flow events across three forest watersheds, (2) evaluate stream export of Hg and MeHg in relation to specific C fractions to help identify shifting sources and controls on Hg mobility, and (3) compare fluxes of Hg species and organic matter across sites and seasons.

2. Methods

2.1. Study Watersheds

2.1.1. Hubbard Brook Experimental Forest

[11] The Hubbard Brook Experimental Forest (HBEF) is in the southern White Mountain region of north-central New Hampshire (43°56'N, 71°45'W) (Figure 1a). Samples were taken from Watershed 6 (W6), the biogeochemical reference watershed at the HBEF [Likens and Bormann, 1995]. Watershed 6 has an area of 13 ha and ranges in elevation from 540 to 800 m. Stream water discharge is measured using a San Dimas flume V-notch weir (www.hubbardbrook.org/watersheds/watersheds.htm). The underlying bedrock of W6 is dominated by the Silurian Rangely formation (sillimanite-grade pelitic schists) and the Kinsman formation (quartz monzonite). The soils are well-drained Spodosols, mostly Haplorthod [Johnson *et al.*, 2000]. The average annual precipitation at the HBEF is ~1400 mm, and the mean annual temperature is 5.6°C. The vegetation of the upper portion of W6 is dominated by red spruce (*Picea rubens* Sarg.), balsam fir (*Abies balsamea* L.), and white birch (*Betula papyrifera* var. *cordifolia* Marsh.). The vegetation of the lower half of the watershed is dominated by sugar maple (*Acer saccharum* Marsh.), yellow birch (*Betula alleghaniensis* Britt.), and American beech (*Fagus grandifolia* Ehrh.).

2.1.2. Sleepers River

[12] The Sleepers River watershed is located in northeastern Vermont (44°30'N, 72°10'W) (Figure 1a). This study was conducted in watershed 9 (W9) at Sleepers River (hereafter referred to as Sleepers). Watershed 9 has an area of 41 ha and ranges in elevation from 519 to 686 m.

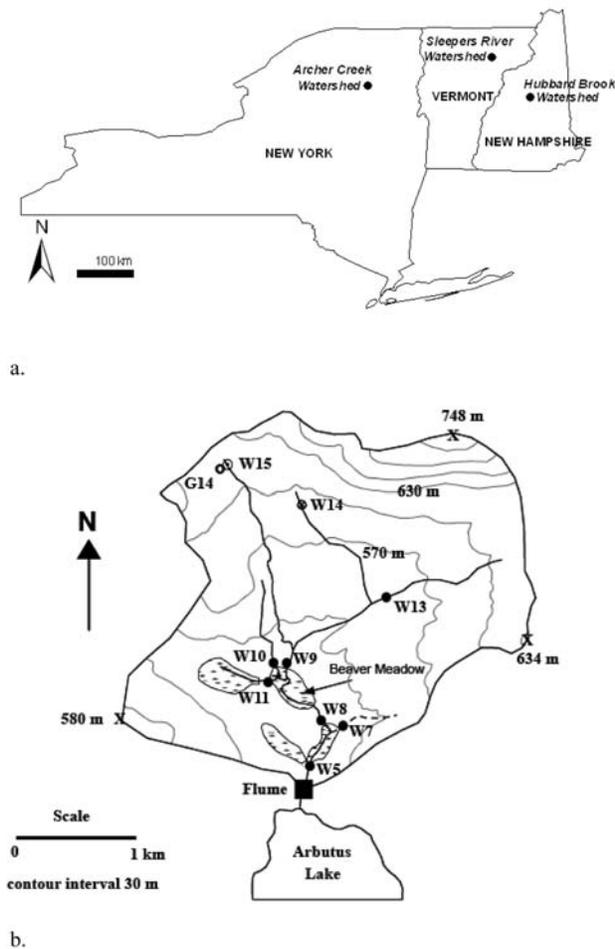


Figure 1. (a) Map showing the three locations of the study watersheds. (b) Map showing the two sample locations on Archer Creek [from *Selvendiran et al.*, 2008b]. The Beaver Meadow sampling location is at W9 and the Lake Inlet sampling location is just above the weir at W5.

Streamflow is measured with a broad-crested V-notch weir. Watershed 9 is a forested, calcareous catchment with areas of poor drainage supporting small wetlands, peat, and mucky riparian soils [*Shanley et al.*, 2004]. The catchment is underlain by the Waits River Formation, a sulfidic calcareous granulite interbedded with micaceous phyllites and biotite schists that generates neutral pH, calcium-bicarbonate-sulfate waters [*Hall*, 1959; *Bailey et al.*, 2004; *Mitchell et al.*, 2008]. The average annual precipitation at Sleepers is ~1200 mm, and the mean annual temperature is 4.6°C. The forest vegetation is primarily northern hardwoods, dominated by sugar maple, yellow birch, white ash (*Fraxinus Americana* L.), and a small population of American beech (*Fagus grandifolia* Ehrh.). Spruce and fir comprise <5 % of the total basal area [*Mitchell et al.*, 2008].

2.1.3. Archer Creek

[13] The Arbutus Lake Watershed (ALW) at the Huntington Wildlife Forest is located in the central Adirondack Mountain region of New York (43°59'N, 74°14'W) (Figure 1a). The ALW ranges in elevation from

513 to 748 m. Our study site was the Archer Creek catchment which has an area of 135 ha and is gauged with an H-Flume. Water samples were collected at two locations from Archer Creek (Beaver Meadow site (65 ha) and Lake Inlet site (135 ha)) in the ALW (Figure 1b). There are two wetlands located between the upper Beaver Meadow site and the lower Lake Inlet site that comprise ~4% of the overall ALW area. The upper wetland is an abandoned beaver meadow covered by grasses, sedges, and some *Sphagnum* ssp. and the lower wetland is a riparian peatland with an overstory consisting primarily of speckled alder (*Alnus incana* L.) [*Bushey et al.*, 2008]. The soils of both wetlands are Greenwood mucky peat [*Bushey et al.*, 2008; *Mitchell et al.*, 2008]. The bedrock at the ALW is dominated by granitic gneiss, and the upland soils are largely Typic Haplorthods in the Beckett-Mundal series. The annual precipitation at the ALW is ~1300 mm, and the mean annual temperature is 4.4°C. The ALW vegetation consists primarily of northern hardwood forest dominated by American beech and sugar maple at higher and midelevations. At lower elevations mixed hardwood-conifer stands dominate with eastern hemlock (*Tsuga Canadensis* L.), red spruce, and some balsam fir scattered throughout. The ALW watershed is intermediate in drainage class of the three sites.

2.2. Sample Collection

[14] Stream samples were collected for Hg and organic matter analyses at each site from September 2005 to July 2007, with greater frequency during high flow periods (snowmelt and precipitation events) (Figure 2). Higher flow conditions were targeted for sampling because a significant portion of the annual water and chemical fluxes from a watershed occur during high flow periods, particularly for solutes such as Hg whose concentrations increase with increasing flow. Samples for Hg analyses were collected in duplicate in new PETG 500 mL bottles using clean procedures [*USEPA*, 1996]. Bottles were rinsed three times with stream water prior to sample collection. Samples were preserved with 0.4% trace metal grade hydrochloric (HCl) acid and stored in double polyethylene bags at 4°C for Hg analysis. One bottle from each of the duplicate samples was filtered using a polyethersulfone filter (0.45 μm) prior to acid preservation for the analysis of dissolved Hg. Samples for DOC concentration and fractionation were filtered in the field through Gelman AquaPrep 600 capsule filters™ (0.45 μm). The capsule filters were rinsed with sample water prior to collecting the sample. Samples were filtered into three 1 L, precombusted, amber glass bottles with Teflon lined caps for fractionation, and into one 125 mL, precombusted, amber glass bottle with Teflon lined cap for DOC concentration and UV absorbance measurements. Samples were collected for suspended sediment concentration (SSC) and particulate organic carbon (POC) analyses in a 1 L polyethylene bottle. A second 1 L stream sample was collected in a polyethylene bottle for the remaining chemical analyses. Samples were shipped overnight on ice to Syracuse University (NY) for Hg and ancillary water chemistry analyses, and to the US Geological Survey laboratory in Boulder, Colo, for DOC fractionation and ultraviolet (UV) absorbance measurements. Samples were refrigerated and stored in the dark at both laboratories at 4°C.

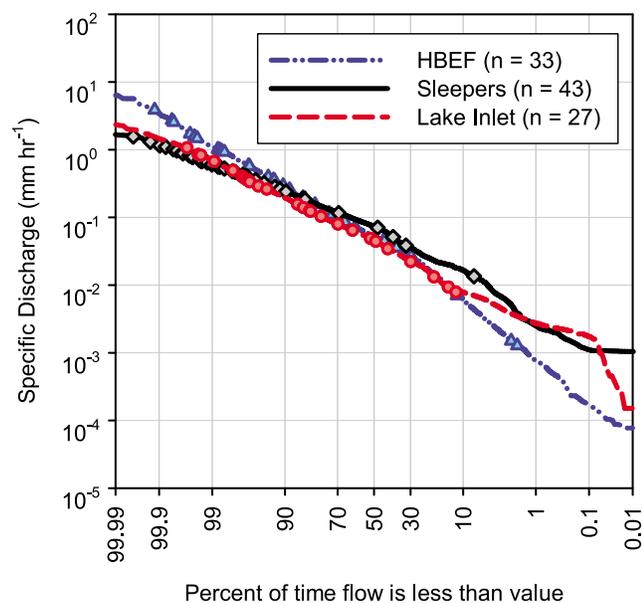


Figure 2. Flow duration curves for the HBEF, Sleepers, and Lake Inlet from 1 January 2005 to 31 December 2007. Points on the line represent samples collected. (Note: Beaver Meadow $n = 25$ and is not shown because it is a sampling point located directly upstream from Lake Inlet, and both sites were sampled at the same time (with the exception of two snowmelt samples) and under the same flow conditions) (note \log_{10} scale on y axis).

2.3. Chemical Analyses

[15] Cation (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and silica (SiO_2) concentrations were determined using inductively coupled plasma-mass spectroscopy (Perkin Elmer ELAN 6100, Perkin Elmer Inc., Waltham, Mass) in accordance with USEPA method 200.8 [USEPA, 1994]. Samples for SSC and POC analysis were collected on preweighed glass fiber filters ($0.7 \mu\text{m}$, prebaked at 450°C ; note that $0.7 \mu\text{m}$ is the minimum pore size for GFF filters, which were selected so that filters could be precombusted to remove traces of organics). The filters and contents were dried at 103°C for 24 h and weighed to determine SSC. Particulate carbon (PC) was analyzed using high temperature combustion (Costech Elemental Combustion System Model ECS 4010, Costech Analytical Technologies, Valencia, Calif). It was assumed that particulate inorganic carbon is negligible compared to POC in these soft waters [Keefe, 1994]; thus, PC was assumed to represent POC on all samples.

[16] Dissolved organic carbon measurements were performed on an OI Analytical Model 700 TOC analyzer [Aiken et al., 1992]. UV-visible absorbance measurements were performed on a Hewlett-Packard photodiode array spectrophotometer (model 8453) between 200 and 800 nm using a 10 mm quartz cell. All sample spectra were referenced to a blank spectrum of distilled water. To minimize temperature effects, all samples were allowed to reach laboratory temperature prior to measurement. Specific ultraviolet absorbance (SUVA_{254}) values were determined by dividing the UV absorbance measured at $\lambda = 254 \text{ nm}$ by the DOC concentration and are reported in units of liter per milligram carbon per meter [Weishaar et al., 2003]. SUVA_{254}

is commonly used as an indicator of DOC aromaticity [Chin et al., 1994; Weishaar et al., 2003]. The fluorescence index (FI), an optical parameter related to DOC source and composition [McKnight et al., 2001], was determined on a subset of samples from each site (Sleepers, $n = 8$; HBEF, $n = 12$; Beaver Meadow, $n = 8$; and Lake Inlet, $n = 10$) using 3-D fluorescence matrices obtained using a Horiba Jobin-Yvon Fluoromax®-3 spectrofluorometer according to methods described by McKnight et al. [2001]. Finally, the hydrophobic organic acid fraction (HPOA) of the DOC was quantified following the procedures by Aiken et al. [1992]. In brief, samples were acidified to pH 2 using HCl and passed through an XAD-8 resin. The HPOA fraction was retained on the XAD-8 resin and then back eluted with 0.1 M NaOH. The eluate was desalted, hydrogen ion saturated, and lyophilized. The HPOA fraction is generally composed of 90%–95% fulvic acid with the remainder being humic acid.

[17] Water samples were analyzed for THg utilizing automated oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS) (Tekran 2600; Tekran, Toronto, ON, Canada) following US EPA method 1631, revision E [USEPA, 2002]. The concentration of MeHg was determined utilizing distillation, aqueous ethylation, purge and trap, desorption, and CVAFS detection (Tekran 2500; Tekran, Toronto, ON, Canada; Perkin Elmer Clarus 500 Gas Chromatograph; Perkin Elmer, Inc., Waltham, Mass) following US EPA method 1630 [USEPA, 2001]. The concentration of particulate bound THg (PTHg) was estimated by subtracting the filtered THg (FTHg) concentration from the unfiltered THg concentration ($\text{PTHg} = \text{THg} - \text{FTHg}$), and the concentration of PMeHg was estimated by subtracting the filtered MeHg (FMeHg) concentration from the MeHg concentration ($\text{PMeHg} = \text{MeHg} - \text{FMeHg}$). Because particulate concentrations are determined by difference, there is more inherent error than in a single analytical Hg determination.

[18] Partition coefficients were calculated for Hg (II) and MeHg in stream water. Hg (II) was calculated as $\text{THg} - \text{MeHg}$. The partition coefficient (K_d) describes the affinity for Hg (II) or MeHg for their respective particulate phases. Partition coefficients for Hg in surface water are calculated as the ratio of sorbed Hg (PTHg) concentration (ng kg^{-1}) to dissolved Hg (FTHg) concentration (ng L^{-1}) and for MeHg as the ratio of PMeHg (ng kg^{-1}) to FMeHg (ng L^{-1}).

$$K_d = \frac{\text{PTHg}}{\text{FTHg}} (\text{L kg}^{-1}) \quad K_d = \frac{\text{PMeHg}}{\text{FMeHg}} (\text{L kg}^{-1}).$$

2.4. Quality Control and Quality Assurance

[19] Water chemistry quality control included field blanks and duplicates, procedural method blanks and sample duplicates, matrix spike, and matrix spike duplicates. Instrument performance and stability during analysis were evaluated with initial and ongoing precision recovery, instrument detection limit check standards, and verification of independent primary and secondary source standards. The accuracy and precision of the spikes and standards were maintained within 10%, the acceptable recoveries for the method guidelines.

2.5. Statistical Analysis

[20] All statistical procedures were performed using SAS Institute's software (Statistical Analysis Software, version 9.1, 2007; SAS Institute Inc., Cary, NC). Descriptive statistics (i.e., mean, standard deviation (SD), minimum, maximum) were calculated for measured water chemistry parameters and then compared across study sites. A one-way analysis of variance (ANOVA) was performed to determine if there were statistically significant differences ($\alpha = 0.05$) in THg, MeHg, DOC, POC, and SSC concentrations among sites. SAS PROC REG was used for linear regression analysis. Standardized residual plots of the final regression models were examined to satisfy assumptions of homoscedasticity and normality.

2.6. Stream Hg and Organic Matter Flux Calculations

[21] Stream flow was recorded every 5 to 15 min for each watershed. Discharge at the Beaver Meadow site at the ALW was not measured directly but was prorated based on watershed drainage area and measured discharge at the Lake Inlet site. Flow duration curves were constructed for each watershed based on 3 years of discharge data (2005–2007). Fluxes of Hg species and organic matter were estimated by multiplying cumulative flow over the sampling interval by measured stream water concentration. Fluxes of solutes were estimated at each of our sites based on a water year (1 August to 31 July) and also for the dormant season (1 November to 30 April) and growing season (1 May to 30 October). We also exploited the strong correlation between FTHg and discharge (see below Figure 6) to predict FTHg concentration at each site on an hourly basis using regression analysis. The predicted FTHg concentrations were transformed into predicted FTHG flux by multiplying the predicted FTHg concentration by flow. The predicted FTHg fluxes based on concentration–discharge relationships were then compared to FTHg flux at each site based on measured concentration.

3. Results

3.1. Hydrology

[22] Stream samples were collected to capture a range of high flow conditions (different event types, different timing within events) as well as different base flow and seasonal conditions. Flow duration curves were constructed to compare the hydrologic responses of the three streams (Figure 2). The sampling regime for this study was intentionally biased toward high flow events, with more than half of the samples taken at each site in the upper 10% of the flow distribution (Figure 2). The remaining samples were collected across the hydrographs to adequately capture both base flow conditions and medium flow events. The three sites had similar flow distributions in the 10%–90% flow range (Figure 2). The HBEF had lower base flow and was also somewhat flashier than the other two sites, with greater maximum flow in the upper 1% of the flow distribution.

[23] At all sites, a greater percentage of the annual water flux (2005–2007) occurred during the dormant season (HBEF = 61%; Sleepers = 60%; Lake Inlet = 70%; note: Beaver Meadow is directly upstream from Lake Inlet). Of the 3 years of discharge data (i.e., calendar years 2005, 2006, and 2007), the greatest annual stream discharge (mm yr^{-1})

occurred at Sleepers (1043) and Lake Inlet (820) in 2006 and in 2005 at the HBEF (1155). At all of the sites, the lowest annual stream discharge (mm yr^{-1}) occurred in calendar year 2007 (HBEF = 879; Sleepers = 837; Lake Inlet = 603).

3.2. Hg and DOC Dynamics

[24] The study sites represent a gradient of stream Hg and organic matter concentrations. In general, Sleepers River was characterized by higher THg and PTHg concentrations and greater variability in most measurements relative to the other three sites (Figure 3). The HBEF had low THg and DOC concentrations. Of the two sites located on Archer Creek, Beaver Meadow was intermediate in THg, DOC, and POC concentrations, while Lake Inlet was characterized by higher DOC and FMeHg concentrations (Figure 3).

[25] Total Hg concentrations (unfiltered samples) were greatest at Sleepers (Figure 3), with maximum values up to 76 ng L^{-1} . The other three sites had lower THg concentrations and were not significantly different from one another ($P > 0.05$). The FTHg concentrations were lower at the HBEF site, compared to the other three sites. Mean PTHg concentration was greatest at Sleepers River (12.9 ng L^{-1} SD = 16.5) compared to the HBEF (0.6 ng L^{-1} SD = 0.7), Beaver Meadow (0.9 ng L^{-1} SD = 1.6), and Lake Inlet (0.8 ng L^{-1} SD = 0.7). At Sleepers, which contained the greatest concentrations of POC, ~74% of THg occurred as PTHg. For the other three sites, PTHg was also a substantial percentage of THg (21%–33%); however, FTHg was the major fraction of THg. Partitioning coefficients for Hg (II) were similar across sites (range of mean $\log_{10} K_d = 5.33$ – 5.59), except for lower values at Sleepers (mean $\log_{10} K_d = 4.97$).

[26] Mean MeHg concentrations (unfiltered samples) were low (0.03 ng L^{-1}) and statistically similar at the HBEF (SD = 0.02) and Beaver Meadow (SD = 0.02) sites. Higher MeHg concentrations were measured at Lake Inlet (0.14 ng L^{-1} SD = 0.09) and Sleepers (0.21 ng L^{-1} SD = 0.28). The percent MeHg of THg (%MeHg) varied within site; however, mean and ranges of %MeHg were similar across sites. The %MeHg ranged from 0.7% to 11.6% (mean = 3.4%; SD = 2.4) at the HBEF, at Sleepers from <0.1% to 11.9% (mean = 2.2%; SD = 2.0), at Beaver Meadow from <0.1% to 9.5% (mean = 2.1%; SD = 2.1), and at Lake Inlet from 0.4% to 12.0% (mean = 4.2%; SD = 2.3).

[27] Mean FMeHg concentrations were low (0.02 – 0.03 ng L^{-1}) and statistically similar ($P > 0.05$) at the HBEF (SD = 0.01), Sleepers (SD = 0.03), and Beaver Meadow (SD = 0.02) sites. Lake Inlet had significantly higher ($P < 0.05$) mean FMeHg concentration (0.11 ng L^{-1} SD = 0.09) compared to the other sites. Mean PMeHg concentrations were low at the HBEF and Beaver Meadow ($<0.02 \text{ ng L}^{-1}$ SD < 0.02) and Lake Inlet (0.04 ng L^{-1} SD = 0.05) compared to Sleepers (0.18 ng L^{-1} SD = 0.26). Partitioning coefficients for MeHg were also similar across sites (range of mean $\log_{10} K_d = 5.58$ – 5.95), with the exception of lower K_d at Sleepers (mean $\log_{10} K_d = 4.71$). Pooling the data across all sites, there was a significant ($P < 0.05$) correlation between FTHg and DOC concentration ($r^2 = 0.87$) (Figure 4) and a stronger correlation between the concentrations of the HPOA fraction of DOC and FTHg ($r^2 = 0.91$). The UV_{254} absorbance was an even stronger predictor of FTHg concentration than DOC or HPOA ($r^2 = 0.92$). There was a strong positive correlation between the UV_{254}

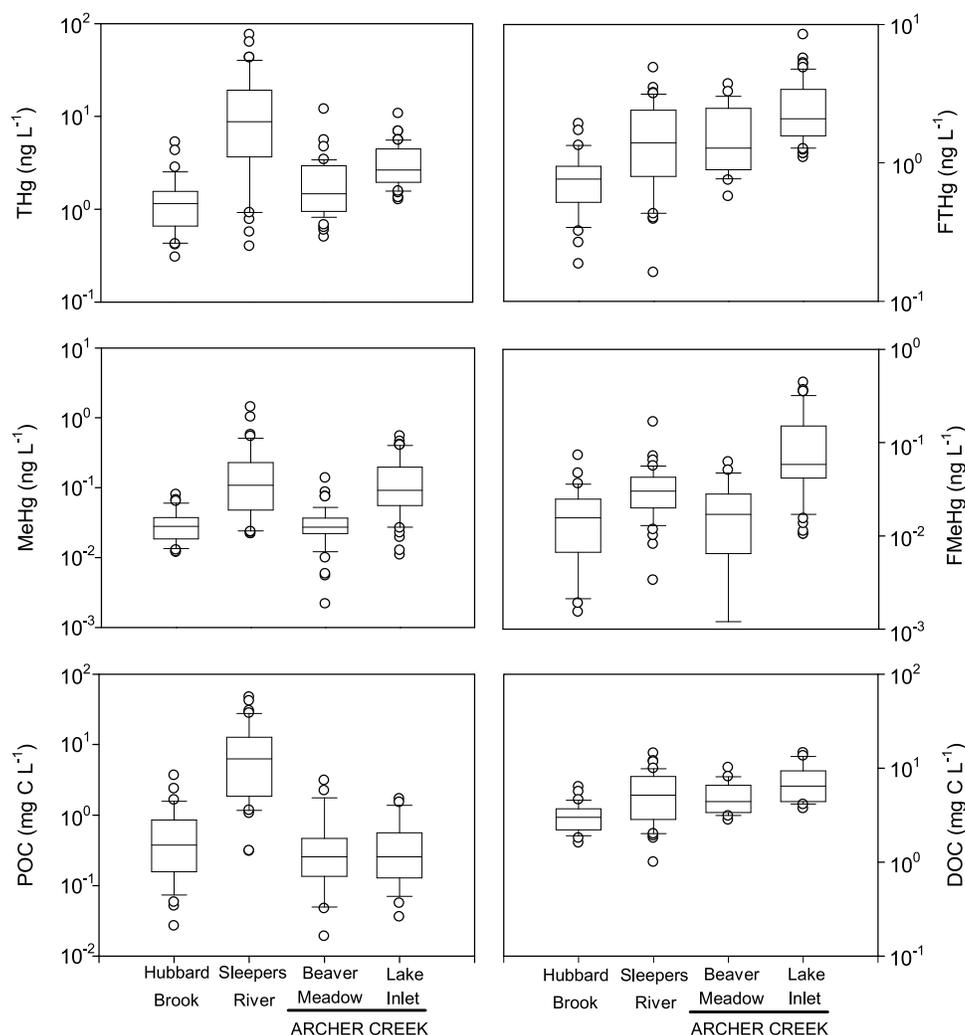


Figure 3. Box plots showing ranges for total mercury (THg), filtered THg (FTHg), methyl mercury (MeHg), filtered methyl mercury (FMeHg), dissolved organic carbon (DOC), and particulate organic carbon (POC) at each study site. The horizontal bars within the boxes are median values; top and bottom are 25th and 75th percentile values, vertical lines extending from the box are the 10th and 90th percentile values, and open circles represent individual values at the extremes of the range (note \log_{10} scale on y axis, and different ranges for unfiltered and filtered THg and MeHg).

absorbance of the DOC and the amount (expressed as mg C/L) of the HPOA ($r^2 = 0.98$). Across sites, the HPOA fraction comprised from 49%–57% of the total DOC. The PTHg concentrations were positively correlated ($P < 0.05$) with POC concentration ($r^2 = 0.56$) (Figure 5). Across sites, POC concentration was also positively correlated with SSC ($r^2 = 0.81$) and likewise the PTHg concentration was positively correlated ($P < 0.05$) with SSC ($r^2 = 0.56$). Both Hg (II) and MeHg partitioning coefficients ($\log_{10} K_d$) were negatively correlated to \log_{10} SSC (Hg (II)-SSC ($r^2 = 0.67$; $P < 0.05$)) and MeHg-SSC ($r^2 = 0.60$; $P < 0.05$).

[28] SUVA, a surrogate for DOC aromaticity, was greatest at Lake Inlet (mean = 2.8; SD = 0.2; range = 2.4–3.3) and followed a similar pattern as DOC concentration (Figure 3) with progressively lower SUVA at Beaver Meadow (mean = 3.3; SD = 0.3; range = 2.6–3.9), Sleepers River (mean = 3.3; SD = 0.4; range = 1.9–3.9), and HBEF (mean = 2.8; SD = 0.3; range = 2.4–3.3). SUVA was positively correlated to the

FTHg ($r^2 = 0.53$; $P < 0.05$) and the HPOA fraction of DOC ($r^2 = 0.45$; $P < 0.05$). The fluorescence index (FI) was determined for a subset of samples at each site. The HBEF had the greatest FI (mean FI = 1.54; SD = 0.05; range = 1.46–1.62), followed by Beaver Meadow (mean FI = 1.35; SD = 0.04; range = 1.29–1.38) and Sleepers River (mean FI = 1.33; SD = 0.05; range = 1.28–1.42), with the lowest FI at the Lake Inlet site (mean FI = 1.28; SD = 0.03; range = 1.24–1.32). In addition to having the lowest FI, Lake Inlet was also the site with the greatest SUVA, suggesting that DOC quality was influenced by the large wetland directly upstream. The range of FI at our sites indicates that most of the organic carbon originates from terrestrial material (i.e., allochthonous inputs). However, note that most of our sampling efforts focused on high flow events. Across all sites, the FI was negatively correlated to the HPOA concentration of DOC ($r^2 = 0.48$; $P < 0.05$) and to SUVA ($r^2 = 0.61$; $P < 0.05$).

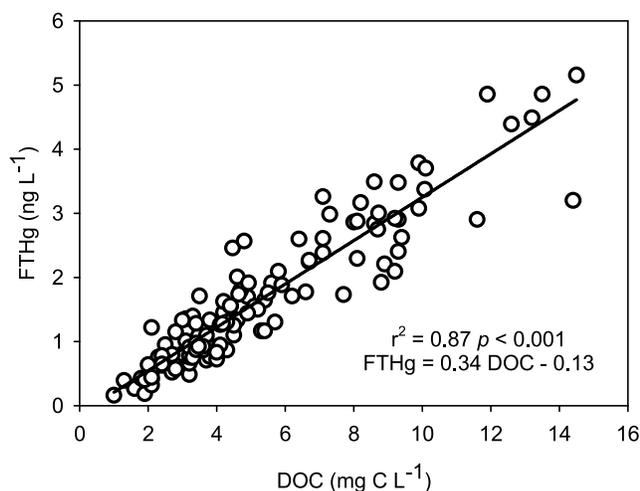


Figure 4. Filtered total mercury (FTHg) concentration (ng L^{-1}) as a function of DOC concentration (mg C L^{-1}) for all stream water samples collected across watersheds.

[29] Unlike THg, MeHg was poorly related to DOC, HPOA, SUVA, and UV_{254} . Likewise, we found no significant relationships between MeHg and other ancillary chemistry (e.g., pH, SO_4^{2-}).

3.3. Discharge and Water Chemistry

[30] Stream discharge was an important factor regulating water chemistry. Combining data across sites, cation concentrations (with the exception of K^+) and SiO_2 were negatively correlated to discharge (Na^+ , $r^2 = 0.33$; Ca^{2+} , $r^2 = 0.30$; Mg^{2+} , $r^2 = 0.21$; SiO_2 , $r^2 = 0.28$). Suspended sediment concentration (SSC) and POC concentrations were positively correlated with stream discharge with the exception of Lake Inlet (SSC, $r^2 = 0.25$; POC, $r^2 = 0.32$). The regression slopes for SSC-POC and discharge were greater at Sleepers, indicating a greater particulate load per unit discharge compared to the other sites. The relationship between DOC and discharge was weak across sites; however, the relationships were significant for each site. DOC was positively correlated to discharge (HBEF, $r^2 = 0.34$; Sleepers, $r^2 = 0.14$; Beaver Meadow, $r^2 = 0.35$; Lake Inlet, $r^2 = 0.14$). The regression slope for DOC and discharge was greatest at Lake Inlet, consistent with a greater production and transport of DOC at this wetland influenced site. The relationship between HPOA and discharge was also positively correlated by site (HBEF, $r^2 = 0.50$; Sleepers, $r^2 = 0.22$; Beaver Meadow, $r^2 = 0.52$; Lake Inlet, $r^2 = 0.32$). SUVA was positively correlated to stream discharge, with the exception of Lake Inlet (HBEF, $r^2 = 0.46$; Sleepers, $r^2 = 0.37$; Beaver Meadow, $r^2 = 0.54$). The FI was negatively correlated with stream discharge (HBEF, $r^2 = 0.49$; Sleepers, $r^2 = 0.87$; Beaver Meadow, $r^2 = 0.34$; Lake Inlet, $r^2 = 0.21$) indicating a shift in soil C source with changes in flow paths.

[31] Similar to DOC, THg and discharge were positively correlated; however, the relationship was site specific. The correlation was greatest at HBEF ($r^2 = 0.70$), followed by Beaver Meadow ($r^2 = 0.46$), Lake Inlet ($r^2 = 0.16$), and Sleepers ($r^2 = 0.14$). The FTHg fraction followed a similar pattern as THg, with a greater r^2 at HBEF ($r^2 = 0.66$), followed by Beaver Meadow ($r^2 = 0.50$), Sleepers ($r^2 = 0.35$),

and Lake Inlet ($r^2 = 0.26$). PTHg, with the exception of Lake Inlet, was also positively correlated to discharge (HBEF, $r^2 = 0.61$; Beaver Meadow, $r^2 = 0.33$; Sleepers, $r^2 = 0.12$). The regression slope for all THg species and discharge was greatest at Sleepers and lowest at HBEF, consistent with the observed pattern of Hg concentrations at these sites. A greater concentration of THg per unit discharge was exported at Sleepers due to high particulate loads in stream water during high flow events. There was no relationship between MeHg and discharge at any of the sites.

[32] There were differences in the seasonal transport mechanism of Hg across sites, with the transport of DOC and FTHg dominating during the growing season (1 May to 30 October) and the transport of POC and PTHg dominating during the dormant season (1 November to 30 April). The correlations of DOC, HPOA, and SUVA with discharge were stronger and the regression slopes greater during the growing season than for the dormant season. A greater slope during the growing season indicates a greater unit of DOC, HPOA, and SUVA per unit discharge than during the dormant season. Concurrent with greater DOC concentrations during the growing season, the correlation between FTHg and discharge was stronger, and regression slopes were greater during the growing season compared to the dormant season, with the exception of the HBEF. Across sites, THg and DOC concentrations were greatest during summer/fall storm events compared to snowmelt and base flow conditions. Distinct temporal patterns between MeHg and discharge were not observed.

3.4. Mercury and DOC Flux

[33] Mercury flux was greatest at Sleepers (Table 1) because of the large flux of PTHg at this site. The growing season and dormant season fluxes of Hg at Sleepers were about equal with slightly more PTHg and MeHg flux during the growing season. Beaver Meadow and HBEF had the lowest fluxes of Hg; however, there were differences between the dissolved and particulate phase fluxes of Hg at each site. At the HBEF, most of the Hg flux occurred in the dissolved phase during the dormant season, consistent with

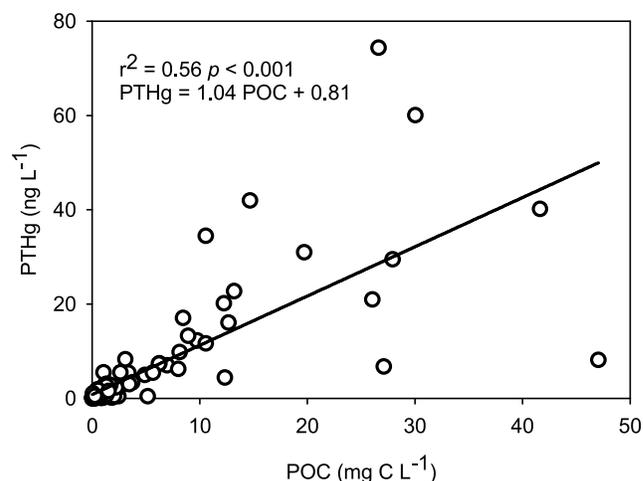


Figure 5. Particulate total mercury (PTHg) concentration (ng L^{-1}) as a function of POC concentration (mg C L^{-1}) for all stream water samples collected across watersheds.

Table 1. Average Fluxes of Total Mercury, Filtered Total Mercury, Particulate Total Mercury, Methylmercury, Filtered Methylmercury, Particulate Methylmercury, Particulate Organic Carbon, Dissolved Organic Carbon, and Hydrophobic Organic Acid Fraction of Dissolved Organic Carbon^a

Site	Season	THg	FTHg	PTHg	MeHg	FMeHg	PMeHg	POC	DOC	HPOA
		$\mu\text{g m}^{-2} \cdot \text{period}^{-1}$						$\text{g C m}^{-2} \cdot \text{period}^{-1}$		
HBEF	GS	0.5	0.3	0.2	0.01	0.01	0.01	0.4	1.4	0.7
	DS	1.3	0.7	0.7	0.02	0.01	0.01	0.6	2.1	1.0
	Annual	1.8	1.0	0.9	0.03	0.02	0.02	1.0	3.5	1.7
Sleepers	GS	3.3	0.9	2.4	0.04	0.01	0.03	2.9	2.3	1.6
	DS	3.2	0.8	2.4	0.04	0.02	0.02	8.8	2.5	1.8
	Annual	6.5	1.7	4.8	0.08	0.03	0.05	11.7	4.8	3.4
Beaver Meadow	GS	0.9	0.7	0.2	0.01	0.01	0.00	0.4	2.2	1.3
	DS	0.7	0.5	0.1	0.01	0.01	0.01	0.1	3.0	1.6
	Annual	1.6	1.2	0.3	0.02	0.02	0.01	0.5	5.2	2.9
Lake Inlet	GS	1.7	1.3	0.4	0.04	0.03	0.01	0.1	3.6	2.1
	DS	1.3	1.0	0.2	0.03	0.02	0.01	0.1	4.6	2.7
	Annual	3.0	2.3	0.6	0.07	0.05	0.02	0.2	8.2	4.8

^aFor the growing period August 2005 to July 2007, for the growing season (GS) (1 May to 30 October), dormant season (DS) (1 November to 30 April), and annual.

a greater flux of DOC. Across sites, the flux of the HPOA fraction of DOC followed a similar seasonal pattern as DOC with greater HPOA flux during the dormant season compared to the growing season (Table 1). Unlike the HBEF, Beaver Meadow had a slightly greater flux of FTHg during the growing season; however, DOC flux, like at HBEF, was greater during the dormant season. This variation may reflect site-specific differences in the transport processes of FTHg between sites. Lake Inlet, which is directly downstream from Beaver Meadow, followed a similar pattern with a slightly greater flux of FTHg during the growing season. Sleepers and Lake Inlet had much greater annual MeHg flux compared to the other sites (Table 1). At Sleepers, the particulate phase of MeHg was responsible for more than half of the annual MeHg flux, in contrast to Lake Inlet where most of the MeHg flux occurred as FMeHg.

[34] There was a strong correlation between FTHg and discharge at each site, unlike the other fractions of Hg and MeHg which were not strongly related to discharge. Therefore, stream water FTHg concentration appears to be closely regulated by stream discharge with observed seasonal (i.e., growing season versus dormant season) variation in both FTHg concentration and discharge. We exploited this strong correlation and developed linear regression models for each study site and season to predict the FTHg concentration (Figure 6 and Table 2). We used the measured stream discharge at each site to predict stream FTHg concentration at an hourly time step. Hourly fluxes of FTHg were then calculated for each site using the predicted FTHg concentration.

[35] The regression model was an effective tool for predicting measured FTHg flux across sites (Table 3). At the HBEF, Beaver Meadow, and Lake Inlet, FTHg fluxes calculated using the concentration-discharge relationship were generally in good agreement with those calculated from the cumulative flow method and differed by at most 20%. At Sleepers, the FTHg flux calculated from concentration-discharge relationships was 40%–50% lower than that calculated by the cumulative flow method. Large peaks in FTHg flux were observed both in summer and fall months

during precipitation events and during the winter and early spring months of snowmelt (Figure 7).

4. Discussion

[36] Studying the biogeochemical response of forested watersheds to hydrologic events (e.g., rainfall, snowmelt) is important for understanding mechanisms of solute transport in forested ecosystems. A significant portion of the annual water and chemical flux from a watershed can occur over a short period during spring snowmelt and storms [Babiarz *et al.*, 1998; Scherbatskoy *et al.*, 1998; Schuster *et al.*, 2008]. Snowmelt and precipitation events can flush pore water from wetlands and upland soil [Hurley *et al.*, 1996; Balogh *et al.*, 1997; Babiarz *et al.*, 1998]. Seasonal differences in watershed hydrology that influence the intensity and duration of high flow periods can have a major influence on solute chemistry [Inamdar and Mitchell, 2004].

4.1. Carbon as a Transport Mechanism for Mercury

[37] The connection of wetlands and riparian areas to streams during hydrologic events can flush stored organic matter and Hg to downstream ecosystems [Schuster *et al.*, 2008; Selvendiran *et al.*, 2008a]. Both dissolved and particulate C play an essential role in the transport of Hg fractions. Across sites, FTHg and FMeHg export closely tracked the gradient of DOC concentrations, with the greatest FTHg and FMeHg export occurring at Lake Inlet, the site with the highest DOC concentration. Mercury concentrations were lowest at the HBEF which is characterized by low concentrations of DOC. The result is in agreement with other studies in the region that report DOC as an important transport mechanism for FTHg [Driscoll *et al.*, 1994, 1995; Selvendiran *et al.*, 2008a; Shanley *et al.*, 2008].

[38] There was a consistent relationship between FTHg and DOC across our sites with about 0.3 ng FTHg per mg of DOC, which is higher than the 0.2 ng Hg per mg DOC reported by Grigal [2002] for sites across the Northern Hemisphere. The similar slopes between our study and those reported by Grigal [2002] for the FTHg-DOC relationship are likely a function of strong correlation between FTHg and

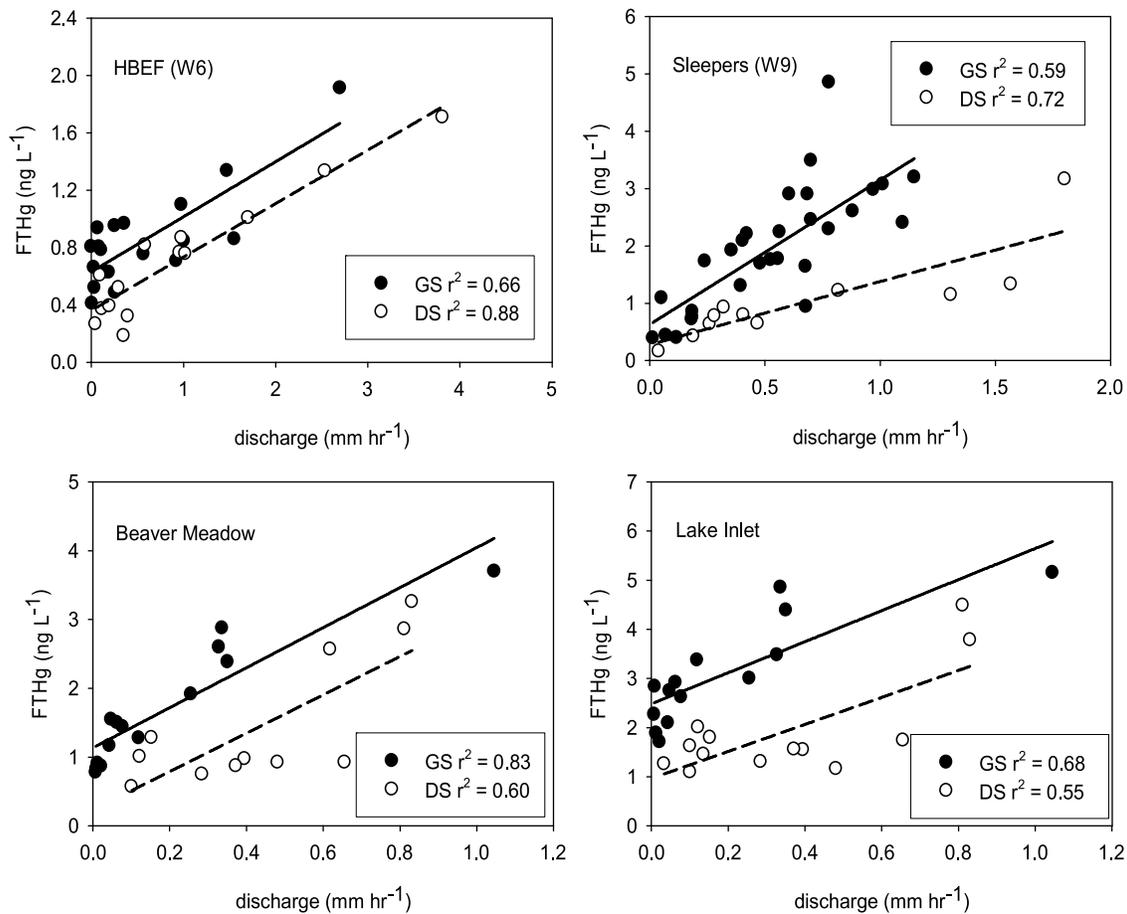


Figure 6. Filtered total mercury (FTHg) concentration (ng L^{-1}) as a function of stream discharge (mm h^{-1}). Open circles represent samples taken during the growing season (GS) months (1 May to 30 October) from 2005 to 2007, and closed circles represent samples taken during the dormant season (DS) months (1 November to 30 April) from 2005 to 2007.

the export of humic material associated with hydrophobic organic matter [Mierle and Ingram, 1991; Grigal, 2002]. Our results suggest that the FTHg is primarily associated with the HPOA fraction of DOC [Dittman et al., 2009], and the HPOA fraction remains a fairly constant percentage (~50%) of the total DOC concentration throughout changes in flow conditions and seasons across our sites. The consistent percent HPOA of DOC and close association of FTHg with the HPOA fraction resulted in similar slopes for the FTHg-DOC relationship across the sites. For sites where HPOA represents a different percentage of the DOC, the slope between the FTHg-DOC relationship would be expected to differ.

[39] The strong correlation across sites between PTHg and POC indicates that transport of Hg in association with POC is important for the export of PTHg, particularly during high flow events when greater amounts of POC were mobilized. Atmospherically deposited Hg is sequestered in forest soils [Lindquist et al., 1991; Astrup et al., 1991; Mason et al., 1994]; therefore, erosion and subsequent downstream cotransport of PTHg, SSC, and POC can be substantial during high flow events [Babiarz et al., 1998; Scherbatskoy et al., 1998]. For example, a significant correlation between THg and the organic fraction of SSC was noted for a forested catchment in northern Vermont

[Scherbatskoy et al., 1998]. The co-transport of Hg and SSC was also significant during storm flow in heavily urbanized watersheds [Mason and Sullivan, 1998].

[40] Both SSC and POC, and in turn PTHg, increase with discharge as in-stream and/or near-stream sediment is

Table 2. Statistics From Simple Regression Models Presented in Figure 4 of Filtered Total Mercury as a Function of Stream Discharge^a

Site	Season ^b	r ²	P	Intercept	SE	β^c	SE
HBEF	GS	0.66	<0.0001	0.63	0.06	0.38	0.07
	DS	0.88	<0.0001	0.36	0.05	0.37	0.04
Sleepers	GS	0.59	<0.0001	0.63	0.25	2.52	0.41
	DS	0.72	0.0010	0.28	0.21	1.10	0.23
Beaver Meadow	GS	0.83	<0.0001	1.13	0.12	2.91	0.38
	DS	0.60	0.0053	0.23	0.39	2.79	0.76
Lake Inlet	GS	0.68	0.0003	2.48	0.21	3.16	0.63
	DS	0.55	0.0039	0.96	0.33	2.75	0.76

^aThe regression models were used to predict FTHg concentration at each site on an hourly basis using measured discharge data from each watershed. Filtered THg is given in nanogram per liter and the stream discharge is given as millimeter per hour.

^bGS indicates growing season (1 May to 30 October); DS indicates dormant season (1 November to 30 April).

^c β is the slope of the regression line.

Table 3. Filtered Total Mercury Flux for the 2005–2006 Water Year (August 2005–July 2006) and Water Year 2006–2007 (August 2006–2007)^a

Site	Cumulative Flow Measured Concentration FTHg Flux		Concentration-Discharge FTHg Flux	
	$(\mu\text{g m}^{-2} \cdot \text{yr}^{-1})$		$(\mu\text{g m}^{-2} \cdot \text{yr}^{-1})$	
	WY 2005–2006	WY 2006–2007	WY 2005–2006	WY 2006–2007
HBEF	1.1	0.9	1.1	0.9
Sleepers	2.0	1.4	1.0	0.8
Beaver Meadow	1.2	0.9	1.2	1.1
Lake Inlet	2.5	1.7	2.1	1.7

^aThe measured flux was calculated based on measured FTHg concentrations and the predicted flux ($\mu\text{g m}^{-2} \text{yr}^{-1}$) was calculated from FTHg concentrations estimated from the concentration-discharge regression relationship (Figure 5). WY, water year.

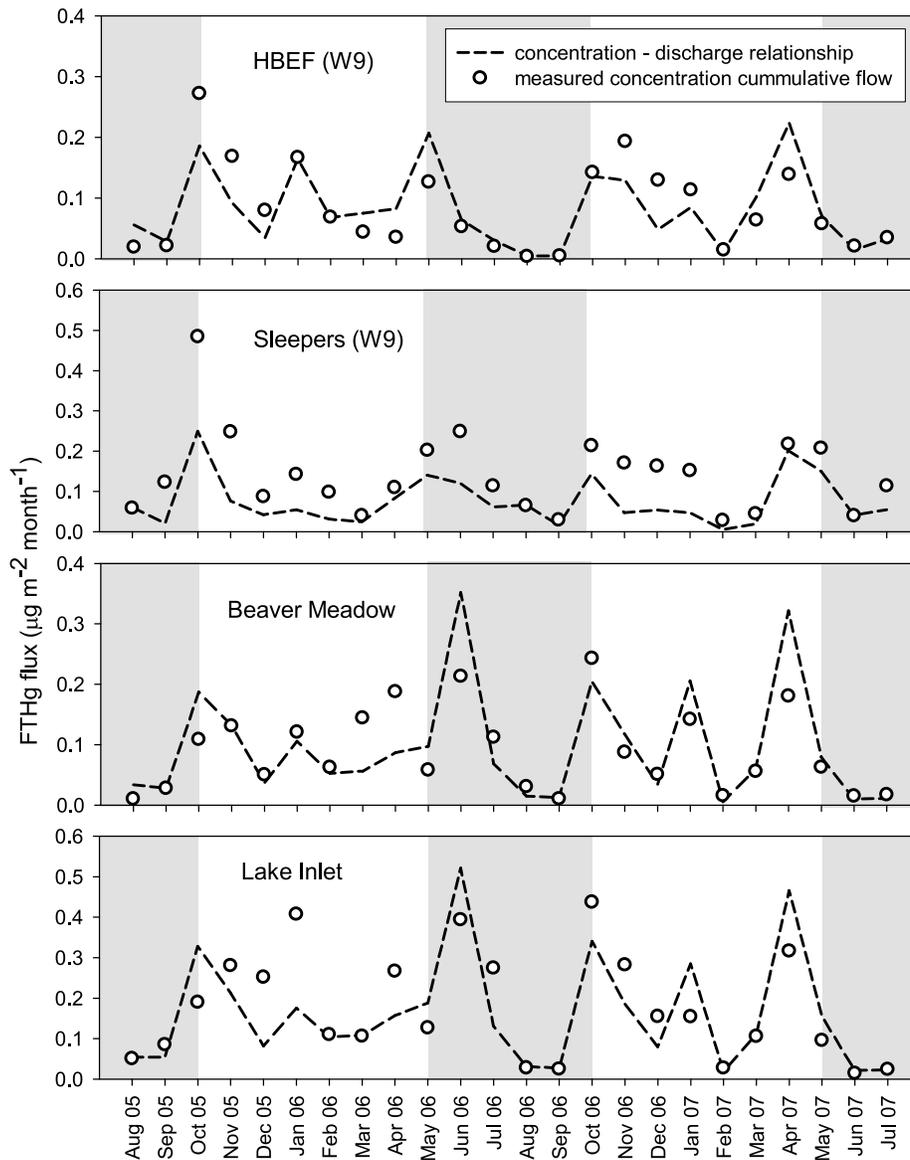


Figure 7. Monthly filtered total mercury (FTHg) flux ($\mu\text{g m}^{-2} \text{month}^{-1}$). The open circles represent FTHg flux based on measured concentrations and cumulative discharge and the dashed line represents the predicted FTHg flux estimated from regression relationships between FTHg concentration (ng L^{-1}) and stream discharge (mm h^{-1}). The shaded area represents the growing season (1 May to 30 October), and the white area represents the dormant season (1 November to 30 April).

eroded during snowmelt and summer storms. The Beaver Meadow site was the only site where POC was not correlated with SSC suggesting that bed sediment also contained variable amounts of inorganic matter. At Sleepers, POC was the primary carrier of THg and MeHg, while at the other three sites, DOC was the primary transport mechanism for THg. Previous studies at Sleepers have also emphasized the importance of PTHg transport in relation to the overall THg flux [Shanley et al., 2002; Shanley et al., 2008].

[41] The range of Hg and MeHg partitioning coefficients (K_d values) were comparable to those reported for Lake Michigan and Wisconsin lakes and rivers [Hurley et al., 1995; Mason and Sullivan, 1998; Babiarz et al., 1998]. The negative correlation between K_d values of Hg (II) and MeHg with SSC are consistent with observations from other streams [Babiarz et al., 1998; Mason et al., 1994; Brigham et al., 2009]. This relationship has been attributed to the “particle concentration effect,” which suggests that lower K_d values with higher SSC are an artifact of increased Hg associated with colloids able to pass through a filter [Babiarz et al., 2001]. Therefore, the mass of colloids able to pass through a filter increases with SSC suggesting that an increase in colloidal Hg (particulate Hg inaccurately attributed to dissolved Hg) and not preferential partitioning to the aqueous phase is responsible for lower K_d values [Babiarz et al., 2001]. Alternatively, the larger particles mobilized at high flow may contain less Hg per unit mass, given that Hg binding is surficial. One or both of these explanations likely accounts for the lower Hg (II) K_d values observed at Sleepers, the site with the greatest SSC.

[42] There were important seasonal differences in both OM and THg concentrations per unit discharge. The greater regression slopes during the growing season of DOC, HPOA, SUVA, and THg as a function of discharge lead to a greater concentration of OM and THg during this period. This pattern is consistent with higher temperatures driving biological activity, increasing decomposition of available organic matter and solubility of DOC during this time of year [Dawson et al., 2008]. Therefore, temperature influences the availability of DOC for transport resulting in greater DOC-discharge slopes during summer/autumn [Dawson et al., 2008], which translates into elevated pulses of FTHg bound to DOC during high flow events. There was also a greater concentration of HPOA and SUVA per unit discharge during the growing season reflecting the greater availability of humic material in the organic soil horizons to be flushed during summer and fall precipitation events. In contrast, greater overall water flux during the dormant season mobilized sediment both in-stream and from riparian zones that accounted for the greater export of PTHg during this time of year. The FTHg fraction bound to DOC dominated during the GS, while PTHg dominated during the dormant season. However, intense precipitation events during the growing season can also mobilize pulses of SSC and PTHg. These results emphasize that the nature of the THg-OC relationship varies with season altering the chemical character of stream water.

4.2. DOC Source and Quality

[43] Across study sites we observed a dilution of SiO_2 and base cation concentrations during periods of increased stream discharge, indicative of a shift in flow paths from

mineral soil and surficial deposits under base flow conditions to upper soil horizons during high flow events [Shanley et al., 2004; Mitchell et al., 2006]. Changes in hydrology and accompanying shifts in flow paths can influence the amount and chemical quality of DOC within a stream [Aiken and Cotsaris, 1995; Vidon et al., 2008]. DOC consists of a complex mixture of organic molecules that vary greatly in molecular weight due to the wide variety of sources and physical, chemical, and microbial DOC degradation processes [McKnight and Aiken, 1998]. DOC concentrations are highest in the organic soil horizons and are attenuated by sorption and transformed by biodegradation as DOC percolates into the mineral soil [Cronan and Aiken, 1985; Aiken and Cotsaris, 1995]. Under base flow, most DOC in stream water is derived from soil water in lower mineral horizons of the soil profile and groundwater from surficial deposits. As flow increases, the source of DOC shifts to upper soil layers richer in aromatic substances [Vidon et al., 2008].

[44] We observed a shift in DOC source and quality with changes in hydrology across sites. With the exception of Lake Inlet, SUVA increased with stream discharge, indicating a shift to DOC with a greater aromaticity in response to shallower flow paths [Hood et al., 2006; Vidon et al., 2008]. The lack of relationship at Lake Inlet is likely a function of the large wetland immediately upstream. The SUVA from Lake Inlet was consistently high (i.e., a small range in SUVA values compared to the other sites), thus, did not vary as much with changes in discharge. The higher SUVA values from Lake Inlet are consistent with other studies reporting higher SUVA from sites that drain wetlands [Ågren et al., 2008].

[45] Aquatic humic substances in organic soil horizons that originate from higher plants have a greater amount of aromatic C than those derived from microbial sources [McKnight and Aiken, 1998]. The increase in SUVA and decrease in FI with increasing discharge indicate a shift in C source to allochthonous (terrestrial) material containing greater amounts of aromatic compounds [McKnight et al., 2001]. The negative correlation between FI and the HPOA concentration is in agreement with the findings of Dilling and Kaiser [2002] who reported that almost all of the aromatic compounds comprising DOC are found in the HPOA fraction. Therefore, as discharge increased, flowpaths shifted as did the source of DOC to upper soil horizons characterized by a greater HPOA fraction with a greater percent aromaticity. The shift in flowpaths to upper soil horizons during high flow events and the strong relationship between DOC and FTHg suggest that the source of FTHg also shifts during events to the upper soil horizons where Hg may be more recently deposited than Hg from the mineral soil and deeper surficial materials.

4.3. DOC Quality and Mercury Concentration

[46] As soils become saturated, interflow mobilizes hydrophobic organic matter rich in humic complexes [Aiken and Cotsaris, 1995]. The UV_{254} of the DOC was a good predictor of the HPOA fraction of DOC and in turn UV_{254} was also an excellent predictor of FTHg concentration due to the strong association of the HPOA fraction with FTHg [Dittman et al., 2009]. The HPOA fraction of DOC may have a stronger influence on the fate and transport of FTHg than other DOC fractions [Ravichandran et al., 1999;

Haitzer *et al.*, 2003]. The stream water export of FTHg is strongly correlated to the export of humic material associated with hydrophobic organic matter [Mierle and Ingram, 1991; Grigal, 2002]. The HPOA fraction appears to have a greater capacity to bind Hg (II) because of its greater reduced S content compared to other DOC fractions [Haitzer *et al.*, 2003]. Reduced organic S moieties in DOC can be a by-product of mineralization of litter and soil organic matter and strongly bind Hg (II). Higher concentrations of reduced organic S occur where SO_4^{2-} reduction occurs in soils and sediments [Skylberg *et al.*, 2000].

4.4. Methylmercury Export From Uplands

[47] Wetlands, riparian areas, and in-stream sediments can sequester THg during low flow periods and under periodic reducing conditions can be important areas for methylation mediated by sulfate-reducing bacteria [Allan *et al.*, 2001; Galloway and Branfireun, 2004; Shanley *et al.*, 2008]. As these areas are hydrologically reconnected during large storms and snowmelt, MeHg flux can increase in streams. The methylation zones in uplands may serve as an entry point for MeHg in the aquatic food web and export MeHg to down-gradient ecosystems where it may be assimilated [Shanley *et al.*, 2008].

[48] The highest MeHg concentrations were observed at Lake Inlet and Sleepers; however, there were important differences in the partitioning between the dissolved and particulate phase MeHg at each site. At Lake Inlet, the dissolved phase was the dominant fraction of MeHg export, while at Sleepers, most of the MeHg export occurred in the particulate phase. This pattern is consistent with a greater flux of POC at Sleepers and a greater flux of DOC and HPOA at Lake Inlet. It is unclear whether the greater PMeHg at Sleepers is as available for biota uptake as the elevated concentrations of FMeHg at Lake Inlet. It is likely that FMeHg would have a longer water column residence time and would be more available for uptake and assimilation than PMeHg which would more likely be deposited to sediments. The other two sites, HBEF and Beaver Meadow, had low MeHg concentrations; however, the THg export from these sites may be important for downstream methylation zones.

[49] In contrast to THg, MeHg was not well correlated with discharge or organic matter and appears to exhibit dilution during high flow periods. A similar lack of correlation between MeHg concentration and discharge and organic matter was observed by Schwesig and Matzner [2001], who hypothesized that different factors control the transport of THg and MeHg. Although MeHg did not increase with discharge, the observed concentrations from our catchments are likely highly relevant for aquatic biota.

4.5. Estimates of Dissolved Mercury Flux in Stream Water

[50] The combined interaction of OM with Hg and increased flushing of OM during high flow periods can result in the enhanced transport of Hg to downstream ecosystems. Indeed, Shanley *et al.* [2005] reported that across the northeastern United States, stream discharge alone explained 22% of the variance in stream water THg concentrations. We exploited the strong correlation between FTHg concentration and discharge to predict FTHg flux based on the

concentration-discharge regression (Figure 6). We observed peaks in FTHg flux during April, a month of increased stream flow due to snowmelt, and November, a month following leaf senescence and decreased water uptake by plants. Demers *et al.* [2010] also observed increases in THg concentrations at the HBEF during spring snowmelt. Balogh *et al.* [2002] observed a similar pattern in two prairie streams in south-central Minnesota, with MeHg concentrations peaking in early May (after algal blooms) and in early October (after autumnal leaf fall) concentrations. The wettest year of our study, calendar year 2006, coincided with the greatest annual FTHg flux of the three year study (2005–2007).

[51] The regression relationship between FTHg and discharge was effective in predicting FTHg flux from each watershed. However, note that our sampling regime was strongly weighted toward capturing high flow events; therefore, we were able to capture the wide variations in Hg concentration with discharge. Fixed interval sampling regimes typically fail to capture high flow events leading to underestimates of Hg flux. For example, Selvendiran *et al.* [2008a] reported an annual THg flux, based on monthly sampling, of $2.3 \mu\text{g m}^{-2} \text{yr}^{-1}$ from Lake Inlet compared to the THg flux determined in this study, which included high flow events, of $3.0 \mu\text{g m}^{-2} \text{yr}^{-1}$.

[52] The difficulty in capturing Hg dynamics at a fine temporal scale during inclement weather conditions when high flow events typically occur has led to the development of “proxy” measures of Hg. Optical properties such as UV_{254} absorbance have been demonstrated as effective proxies of FTHg concentrations in stream water [Dittman *et al.*, 2009]. In addition to proxy measurements for FTHg, there is also a need to quantify the PTHg fraction in order to improve estimates of THg flux. Whyte and Kirchner [2000] used the strong correlation ($r = 0.98$) between THg (note: PTHg represented 99.97% of their THg) and SSC to estimate fluxes of THg at an abandoned mine site in northern California. By measuring turbidity using an optical backscatter sensor, Whyte and Kirchner [2000] were able to compute a continuous record of PTHg flux. Combining the two proxy approaches for estimating FTHg and PTHg will allow for the possibility of near-real-time measurements of THg flux. Better estimates of Hg flux will provide an opportunity to better understand Hg dynamics on a fine scale and also allow for more accurate estimates for Hg budgets, also useful for tracking the future recovery of Hg-contaminated ecosystems.

5. Conclusions

[53] These results underscore the importance of monitoring Hg species and organic matter fractions in streams during high flow periods to better quantify Hg dynamics and fluxes from forested watersheds. Shifts in the quality and quantity of OM with increasing discharge influenced the transport processes of Hg across watersheds. Upper soil horizons are rich in aromatic compounds and impart high DOC concentration to infiltrating waters. As soils become saturated, interflow mobilizes hydrophobic organic matter rich in humic substances. Across the three sites of our study, the export of FTHg was strongly correlated to the export of the HPOA fraction of DOC. The export of DOC and FTHg was greatest during the growing season due to warmer temperatures leading to increased biological activity and

processing of organic matter. In comparison, PTHg and POC export dominated during the dormant season likely due to greater mobilization of stream sediments during this time of year.

[54] The co-transport of Hg in association with dissolved and particulate organic matter is important for the export of Hg from the watershed. The PTHg fraction comprised a large percentage of THg at Sleepers, in contrast to the other sites where FTHg comprised the majority of THg. Although MeHg concentrations were variable and not related to organic matter, the observed concentrations of MeHg are highly relevant to aquatic biota. The detectable MeHg concentrations at all sites suggest that methylation zones in uplands serve as an entry point for MeHg in the aquatic food web and that uplands represent an important source of MeHg to downstream ecosystems.

[55] Recent advances in “proxy” measures for THg fractions hold promise for near-real-time monitoring of THg flux. Ultimately, a more detailed watershed(s) Hg monitoring program supplemented with proxy measures is needed to unravel fine temporal scale Hg dynamics and to create more accurate Hg budgets. A better understanding of Hg flux and transport processes will allow for better predictions of future ecosystem response to changes in Hg deposition and climate.

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