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Mercury and Organic Carbon Relationships in Streams Draining Forested Upland/Peatland Watersheds

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ABSTRACT

We determined the fluxes of total mercury (HgT), total organic carbon (TOC), and dissolved organic carbon (DOC) from five upland/peatland watersheds at the watershed outlet. The difference between TOC and DOC was defined as particulate OC (POC). Concentrations of HgT showed moderate to strong relationships with POC (R^2 = 0.77) when all watersheds were grouped. Although POC only accounts for 10 to 20% of the OC transported, we estimate that it is associated with 52 to 80% of the HgT transported from the five watersheds. Total transport of HgT from the watersheds ranged from 0.70 to 2.82 $\mu g\ m^{-2}\ yr^{-1}$. Watershed geometry and hydrology play important roles in determining the influence of OC on HgT transport in forested watersheds. Watershed properties such as peatland area have considerable promise as predictors for estimating HgT transport in streams draining forested watersheds in the Great Lakes States.

THE fate and transport of total mercury (HgT) in terrestrial environments has been little studied and poorly understood. A large knowledge gap currently exists regarding the transport of HgT in and through the terrestrial environment, even though it is widely recognized that terrestrial transport is important in determining loading of atmospherically deposited HgT to the aquatic environment (Lindqvist, 1991). In most watersheds in northern latitudes, peatlands play an important role in cycling of HgT and organic carbon (OC) (Driscoll et al., 1994). In soil systems, HgT and soil organic matter are closely related (Grigal et al., 1994; Roulet and Lucotte, 1995), as are HgT and OC in soil solution (Aastrup et al., 1991). The link continues to the aquatic system. Total Hg is positively correlated with OC in stream/runoff waters (Hurley et al., 1995; Lee and Iverfeldt, 1991; Johansson et al., 1991; Johansson and Iverfeldt, 1994) and in lake waters (Meili et al., 1991; Lee and Iverfeldt, 1991; Driscoll et al., 1994; Driscoll et al., 1995; Sorensen et al., 1990).

It is therefore apparent that OC plays an important role in the watershed cycling of HgT; the hydrological pathways that control the terrestrial transport of OC also influence the terrestrial transport and cycling of HgT (Kolka, 1996). If a close relationship between OC and HgT in solution exists and can be quantified, then predictions of sites and processes associated with enhanced HgT transport will be possible.

Watershed parameters have also shown promise in predicting HgT fluxes and concentrations. Hurley et al. (1995) found correlations with watershed land use (urban, wetland, forest, and agriculture) and HgT for 39 Wisconsin rivers. Driscoll et al. (1995) found that the percentage of near-shore wetlands in a watershed influences HgT concentration in lakes of the Adirondack region of New York. Commonly wetlands, especially peatlands, hold large reserves of OC. Considering wetlands are the source of flow to many surface waters, OC transported from peatlands likely influences HgT transport to lakes and streams. Separating the influence that wetlands and associated uplands have on total watershed cycling of HgT and OC would allow watershed parameters such as wetland area, wetland type, upland/wetland area ratio, or other physically based watershed metrics to be used to predict HgT loading to surface waters.

The objective of this study was to compare and contrast the relationships between HgT and OC concentrations and fluxes from stream waters draining five forested watersheds and assess if watershed parameters influence this relationship.

MATERIALS AND METHODS

Site

The USDA Forest Service Marcell Experimental Forest is a 890-ha tract located 40 km north of Grand Rapids, MN (47°32′N, 93°28′W, Fig. 1). The Marcell Experimental Forest has been reserved for long-term research with the cooperation of the USDA Forest Service North Central Forest Experiment Station, the Chippewa National Forest, Minnesota Department of Natural Resources, Itasca County, and a private landowner. Watersheds at the Marcell Experimental Forest consist of an upland portion and a peatland; the source of a stream leaving the watershed. The peatlands vary from perched bogs with little or no regional groundwater influence to fens with groundwater influence, providing a range of hydrological environments. The landscape of the Marcell Experimental Forest is typical of morainic landscapes in the Upper Great Lakes Region, providing wide applicability of the study. The Marcell Experimental Forest was of particular interest because it has a large historical database concerning hydrology (Nichols and Brown, 1980; Boelter and Verry, 1977) and chemical cycling and transport (Grigal, 1991; Urban et al., 1989; Verry and

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Abbreviations: HgT, total mercury; OC, organic carbon; TOC, total organic carbon; DOC, dissolved organic carbon; POC, particulate organic carbon.

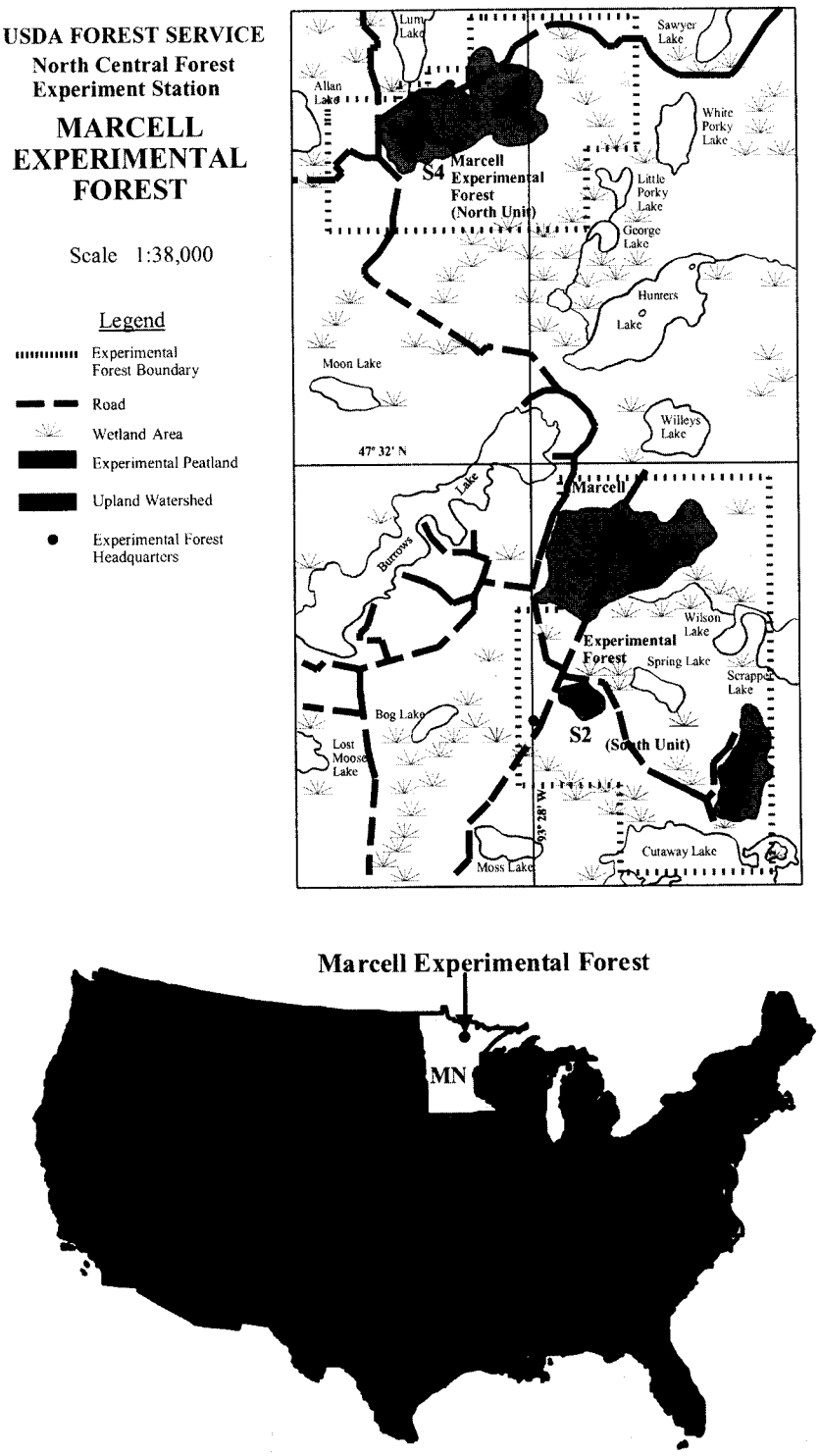

Fig. 1. Location of the Marcell Experimental Forest.

Timmons, 1982; Verry, 1981). Climate and hydrological data have been collected continuously since 1960.

Climate

The climate of the Marcell Experimental Forest is subhumid continental, with wide and rapid diurnal and seasonal temperature fluctuations (Verry et al., 1988). The average annual air temperature is 2°C, with extremes of −46°C and 40°C. Average January and July temperatures are −14°C and 19°C, respectively (Verry, 1984), and average annual precipitation is 77.5 cm with 75% occurring in the snow-free period (mid-April to early November). An average of 65 rainstorms occur each year but normally only three to four exceed 2.5 cm (Verry et al., 1988).

Summary of Watersheds (Table 1)

S1 Watershed. The S1 Watershed contains an 8.1-ha black spruce [*Picea mariana* (Mill.) B.S.P.] bog that was harvested in two successive strip cuts 5 yr apart (1969 and 1974). Currently the bog overstory is dominated by 3-m black spruce

Table 1. Summary information for the five study watersheds at the Marcell Experimental Forest.

Watershed	Peatland type	Upland area	Peatland area	Mean outlet
		ha		pH
S1	Bog	25.1	8.1	4.0
S2	Bog	6.5	3.2	4.0
S3	Fen	121.4	18.6	7.1
S4	Bog	25.9	8.1	4.3
S5	Bog	46.5	6.1	4.4

with a significant component of paper birch (*Betula papyrifera* Marsh.) of similar height. The 25.1-ha upland is dominated by mature trembling aspen (*Populus tremuloides* Michx.) and paper birch. Soils include the Greenwood series (Typic Borohemist) in the bog and the Warba series (Glossic Eutroboralf) in the upland (Soil Survey Staff, 1987). Flow from S1 was not directly monitored during the study. Streamflow was estimated from historic regressions relating S1 and S2 (R^2 = 0.90, p = 0.0001).

S2 Watershed. The S2 Watershed contains a 3.2-ha mature black spruce bog and a 6.5-ha upland dominated by mature trembling aspen and paper birch. The S2 Watershed has been used as a control for studies conducted in other watersheds on the Marcell Experimental Forest and has also been used to study nutrient cycling, peatland dynamics, vegetation communities, CO_2, and CH_4 emissions and various hydrological processes. Soils in the watershed are dominated by the Loxly series (Typic Borosaprist) in the bog and the Warba series in the upland (Soil Survey Staff, 1987). Flow from the S2 Watershed is monitored with a v-notch weir at the outlet. Surface and subsurface runoff are monitored on north- and south-facing slopes of the upland.

S3 Watershed. The S3 Watershed contains an 18.6-ha fen dominated by a 24-yr-old stand of willow (*Salix* spp.), speckled alder [*Alnus rugosa* (DuRoi) Spreng.], black spruce, and paper birch. The entire fen was clearcut in the winter of 1972–1973. The effective contributing area to the fen includes 121.4 ha of upland (Sander, 1971) that consists of a mixed canopy of trembling aspen, paper birch, balsam fir [*Abies balsamea* (L.) Mill.], and red pine (*Pinus resinosa* Ait.). Soils in the fen are dominated by Moose Lake (Typic Borosaprist) and Lupton series (Typic Borohemist) and Menahga (Typic Udipsamment) and Graycalm series (Alfic Udipsamment) in the upland (Soil Survey Staff, 1987). Flow from S3 is not currently being monitored but well levels within the fen were monitored during the study and are related to flow at the outlet (R^2 = 0.99, p = 0.0001).

S4 Watershed. The S4 Watershed contains an 8.1-ha mature black spruce bog and a 25.9-ha upland dominated by a canopy of 25-yr-old trembling aspen and paper birch. The mature aspen–birch upland was cut in 1971 and allowed to regenerate naturally. Soils in the watershed are dominated by the Greenwood series in the bog and the Nashwauk series (Typic Glossoboralf) in the upland (Soil Survey Staff, 1987). Flow records from S4 were not available during the study, but historic monthly flows were related to flows from the S2 Watershed (R^2 = 0.91, p = 0.0001).

S5 Watershed. The S5 Watershed contains a 6.1-ha mature black spruce bog and a 46.5-ha upland with areas of mature and young trembling aspen, paper birch, and balsam fir. The S5 Watershed was used as a control watershed for the previously discussed harvesting study in S4. Soils in the watershed consist of Moose Lake and Lupton series in the bog and Menahga and Nashwauk series in the upland (Soil Survey Staff, 1987). Flow records from S5 were not available during the study, but historic monthly flows were related to flows from the S2 Watershed (R^2 = 0.89, p = 0.0001).

Hydrologic Data Collection and Water Sampling

Flow at the Marcell Experimental Forest usually ceases for 2 to 4 mo during the winter (December–March) providing a hydroperiod of approximately 8 to 10 mo, depending on watershed and the climate of a particular year. Outlet waters were sampled biweekly for four of the watersheds (S1, S2, S4, and S5) for the hydrologic years 1993–1995. A fifth watershed (S3) was added in 1994. Two long-term, upland runoff plots on the S2 Watershed (Warba series) were sampled after every storm that produced runoff. These plots drained only mineral soils. Three subsamples were collected per sampling event, one for the determination of HgT, a second for DOC, and a third for TOC, pH, cations, and anions. Trained USDA Forest Service employees collected all the samples with a modified clean protocol. Sampling was conducted by a single individual with clean polyvinyl chloride gloves and a Teflon ladle. Sample Teflon bottles were washed with a portion of the sample before collection.

Total Mercury and Organic Carbon Analysis

Total Mercury Analysis

Rigorously tested cleaning and analytical procedures were used throughout sample handling and analysis. Total Hg was measured by double amalgamation cold vapor atomic fluorescence spectrometry (CVAFS) (Bloom and Crecelius, 1983). Most samples for HgT determination had bromine monochloride (BrCl) added during sampling and were analyzed within the following few days. Samples not immediately oxidized with BrCl were frozen; BrCl was added directly to frozen samples and digestion occurred while thawing. After BrCl addition, samples were digested overnight on a heated sand bath at 70°C. Before analysis, excess BrCl was reduced by the addition of hydroxylamine hydrochloride (NH_2OH–HCl). Sample aliquots (0.5–100 mL, depending on expected HgT concentration) were added to bubblers and Hg^{2+} was reduced to Hg^0 by 5 mL of SnCl2. The bubblers were purged for 20 min with Hg-free N_2 gas and Hg^0 was collected on the sample gold trap. Sample traps were heated for 4 min at 500°C and Hg^0 was collected on the analytical trap. The analytical trap was then heated for 3 min and Hg^0 passed into the spectrometer, and Hg^0 peak area was recorded by an integrator.

Organic Carbon Analysis

Samples measured for DOC were filtered through 0.7-μm glass fiber filters and analyzed by a standard low-temperature Dohrman DC-80 total OC analyzer. Unfiltered (TOC) stream samples were measured using the same procedure.

Total Mercury/Organic Carbon Quality Control/Quality Assurance

For HgT analysis, all open container operations were conducted under a HEPA filter in a cleanroom. All laboratory analyses were conducted in full cleanroom garb including lint-free coats and hats. The field collection method was compared to the more established dirty hands–clean hands protocol (St. Louis et al., 1994). A set of seven outlet samples collected with both methods showed no significant differences among paired samples (paired t-test = 0.18, p = 0.86). To assess the impact of freezing on HgT concentration, a set of 17 samples were immediately analyzed and compared to a duplicate set that was frozen for 2 mo before analysis. There were no signifi-

cant differences among paired samples (paired t-test = 1.55, p = 0.14). Cleanroom quality, polyvinyl chloride gloves were worn at all times during handling of samples and sampling equipment. All gases were precleaned by gold traps before contact with the sample. Reagents were routinely analyzed and cleaned of HgT to the extent possible and sets of standards and blanks were analyzed several times each day. A minimum of 10% duplicates was included within each sample train. The 120 duplicate sets provided a standard error (SE) of 0.28 ng L^{-1} for a mean concentration of 12.50 ng L^{-1} (2.3%). Spike recoveries ranged from 93 to 106% with a mean of 100.4%.

For OC analysis, a minimum of 10% duplicates were included within each sample train. The mean concentration for all duplicates was 41.4 mg L^{-1}, with a SE of 3.3% (n = 58).

Statistics

Linear and nonlinear regression were used to fit mathematical expressions to the data. Relationships between concentrations and fluxes of HgT and OC tended toward linear relationships, while those relating HgT and OC fluxes to watershed characteristics tended to be nonlinear in nature. Analysis of covariance was used to compare linear regression slopes among watersheds and multiple regression was used to assess watershed influences on HgT and OC concentrations and fluxes.

RESULTS

Total Mercury and Organic Carbon Concentrations

Biweekly concentrations of HgT and OC were converted to volume weighted mean monthly concentrations for each watershed. Total OC and DOC concentrations showed strong seasonal trends for all watersheds

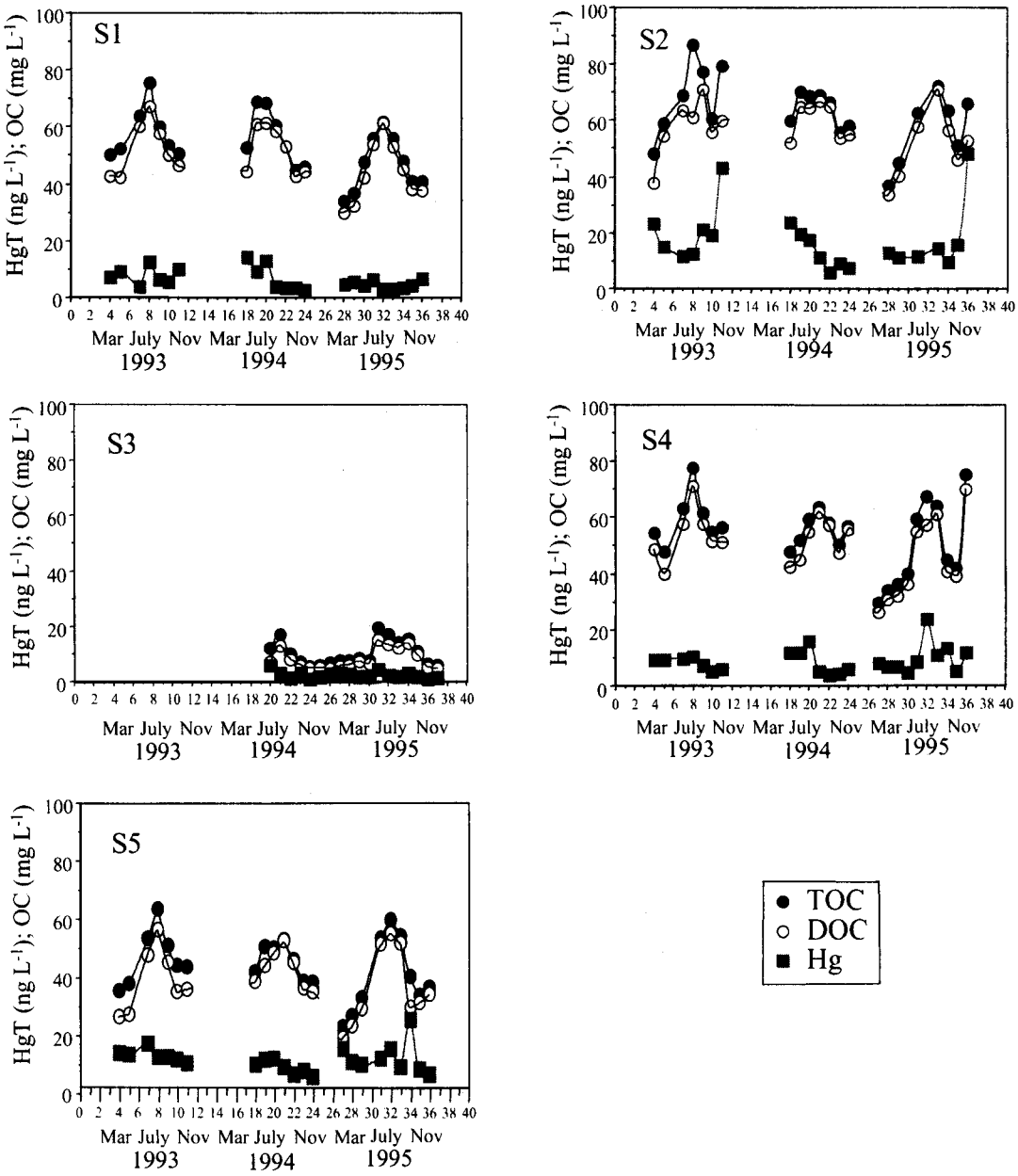

Fig. 2. Mean monthly TOC, DOC, and HgT concentrations for watersheds in the Marcell Experimental Forest.

with peak concentrations during the summer (Fig. 2). Organic C concentrations among bogs (S1, S2, S4, and S5) were similar; however, the groundwater fen (S3) had considerably lower OC concentrations (Fig. 2).

Total Hg concentrations were variable, with annual peak concentrations sometimes associated with peaks in OC (e.g., for S4 in August 1995; Fig. 2) and at other times there was little apparent correlation with either TOC or DOC (e.g., for S2 in July–Sept. 1995; Fig. 2). Correlations (R^2) between monthly HgT and either TOC or DOC did not exceed 40% for any watershed. Although DOC and TOC show annual cycles of concentrations, generally peaking in summer, HgT concentrations are variable, with peaks observed in summer (e.g., for S5 in July 1993; Fig. 2), spring (e.g., for S1 in May 1994; Fig. 2) and fall (e.g., for S2 in November 1993; Fig. 2). Concentrations of DOC for the bog systems (S1, S2, S4, and S5) are generally higher than those in the literature while those for the fen (S3; Fig. 2) are more comparable (11–42 mg L^{-1}, Lee et al., 1995; 2.8–7.8 mg L^{-1}, Krabbenhoft et al., 1995; 11.8–18.6 mg L^{-1}, St. Louis et al., 1994; 3.3–5.4 mg L^{-1}, Mierle, 1990). Although DOC concentrations are higher than those generally reported, stream HgT concentrations are comparable (1.3–7.3 ng L^{-1}, Lee et al., 1995; 2.8–7.8 ng L^{-1}, Krabbenhoft et al., 1995; 5.0–13.1 ng L^{-1}, St. Louis et al., 1994; 2.9–11.2 ng L^{-1}, Westling, 1991; 7.0–8.3 ng L^{-1}, Lee and Iverfeldt, 1991; 1.6–3.2 ng L^{-1}, Mierle, 1990). For all streams for the period of record, HgT concentration averaged 9.1 ng L^{-1}.

It appears from the above results (Fig. 2) that the generation of TOC and DOC is related to temperature and microbial processes; however, other factors are influencing HgT concentrations. Although poor correlations were found between monthly DOC or TOC and HgT, significant positive relationships were found between POC (particulate organic carbon) and HgT (Fig. 3). Particulate OC was operationally defined as the difference between TOC and DOC, or as the fraction of OC > 0.7 μm. When all watersheds and months are grouped, a significant positive relationship continues to exist between HgT and POC (Fig. 3). To our knowledge,

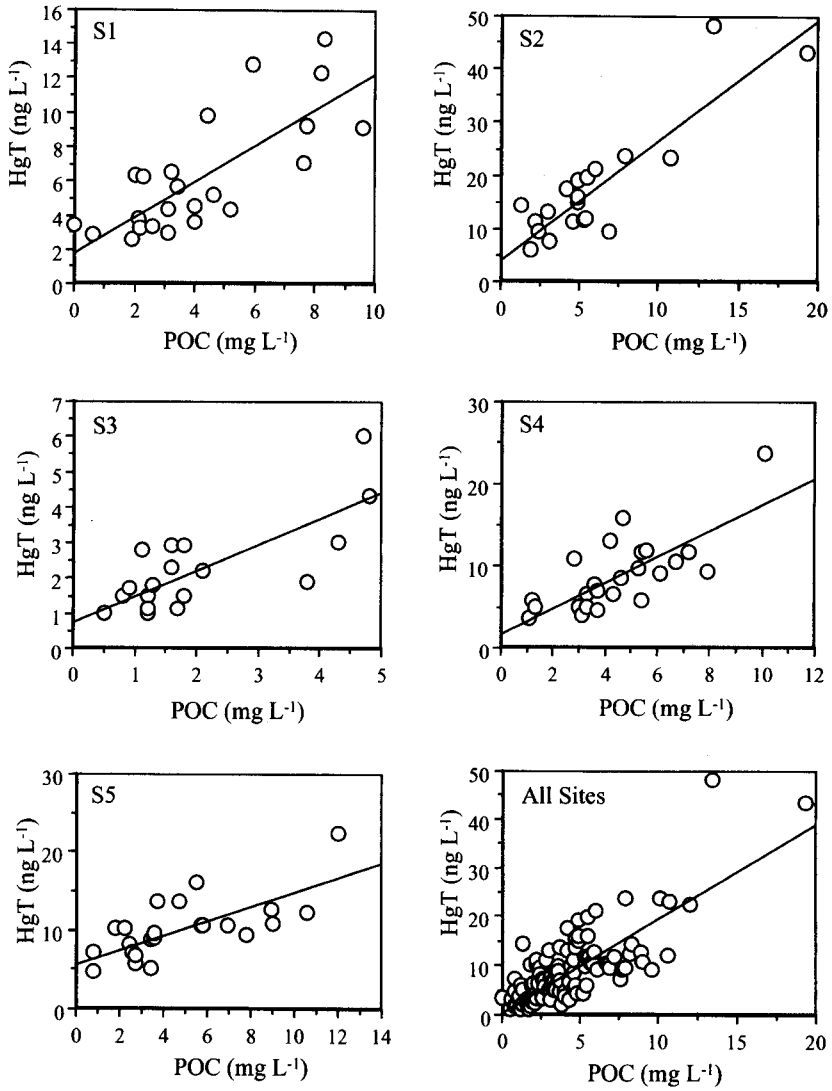

Fig. 3. Relationship between HgT and POC for watersheds in the Marcell Experimental Forest. S1 Watershed, HgT = 1.99 + 1.01(POC), r^2 = 0.58, p = 0.0001. S2 Watershed, HgT = 4.58 + 2.20(POC), r^2 = 0.76, p = 0.0001. S3 Watershed, HgT = 0.82 + 0.71(POC), r^2 = 0.57, p = 0.0003. S4 Watershed, HgT = 1.91 + 1.54(POC), r^2 = 0.54, p = 0.0001. S5 Watershed, HgT = 5.95 + 0.87(POC), r^2 = 0.49, p = 0.0004. All sites, HgT = 0.99 + 1.86(POC), r^2 = 0.60, p = 0.0001. Note differences in scale.

no other study has compared POC and HgT concentrations.

Volume weighted mean monthly HgT concentrations were significantly different among watersheds ($p < 0.001$). Analysis of covariance indicated that the slopes of the HgT–POC relationships for individual watersheds were significantly different from zero ($p < 0.001$) but also different among watersheds ($p < 0.001$). Accounting for the variability that watershed imposed on the overall HgT–POC relationship ($p < 0.001$) increased the explained variation from 0.60 (Fig. 3) to 0.77.

The slope and y-intercept of the HgT–POC relationships for each watershed are important when assessing the sources of HgT in the watershed (Fig. 3). The y-intercept is the concentration of HgT that is associated with DOC or inorganic complexes and the slope represents the ng of HgT associated with each mg of POC. We assume that the HgT not associated with POC is associated with DOC. Since the majority of HgT present in soils occurs as Hg^{2+} and the high affinity of Hg^{2+} for organic matter and soil clays, the ion is not very mobile as a simple salt (Schuster, 1991). Although Cl^- and OH^- both form highly soluble complexes with Hg^{2+} (Schuster, 1991), their relatively low concentrations in most forest soils limit their effectiveness in transport. The HgT associated with DOC (y-intercepts) was regressed upon watershed characteristics (peatland area, upland area, watershed area, and upland/peatland ratio), and was most closely related to the peatland area. As peatland area increases, the HgT associated with DOC decreases (Fig. 4). High production of DOC in peatlands evidently overwhelms the Hg available for transport, decreasing the Hg/DOC ratio. Runoff from uplands, with short residence times and lower DOC, should have higher HgT associated with DOC. In an associated study of upland runoff in the S2 Watershed (Kolka, 1996), we found the HgT associated with DOC to be much higher in upland runoff (10.50 ng L^{-1}) than in stream waters, substantiating our hypothesis (Fig. 4).

Although HgT associated with DOC was most closely related to peatland area, the HgT/POC ratio (i.e., the slope of the relationships in Fig. 3) was more closely related to upland area. As upland area increases, the HgT/POC ratio decreases (Fig. 5). We believe that water residence time and water sources also influence this relationship. We estimated the time of concentration of stormflow waters (Gray, 1973) as a surrogate for water residence time in these watersheds. The time of concentration is the time required for the entire watershed to contribute runoff at the outlet during a storm event. The time of concentration for S2, the smallest watershed, is approximately 50% that of S1, S4, and S5 and approximately 25% that of S3. Particulates derived from the uplands of a large watershed such as S3, have a greater opportunity to settle or become trapped because water flow paths are longer and water residence time is greater than in a smaller watershed such as S2. Although the total particulate load in streams may increase with watershed size, the proportion of HgT in the load decreases because of the greater opportunity for HgT to volatilize or be complexed with more immobile forms of soil OC. If the above hypothesis is true, then the HgT:POC ratio for relatively flashy upland runoff should be higher than that of streams. In the study cited above (Kolka, 1996), we found that to be the case (Fig. 5; 2.59 ng HgT/mg POC).

Poor relationships existed between flow from individual watersheds and either HgT or OC concentrations; none explained >50% of the variation. We found no studies that found a relationship between HgT and flow, although several have correlated flow with OC (Heikkinen, 1990; McDowell and Likens, 1988; Clair and Freedman, 1986; Naiman, 1982). Poor relationships were also found between pH and HgT concentration for individual watersheds; no correlations explained >25% of the variation in HgT. Unlike HgT concentrations, pH for individual watersheds varied little over the duration of our study.

Total Mercury and Organic Carbon Fluxes

Monthly fluxes of HgT and OC were calculated for each watershed, summed annually, and means were calculated for the period of record (Table 2). Although concentrations were low in waters from the groundwater fen (Fig. 3), its high flow results in the greatest fluxes of HgT and OC. The standard error (SE) is the result

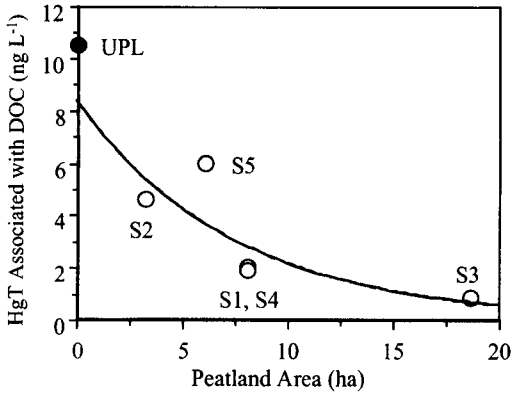

Fig. 4. Relationship between peatland area and the HgT associated with DOC for stream waters at the watershed outlets (HgT = 7.03 × 10 $^{(-0.052 \times \text{Peatland Area})}$, $r^2 = 0.79$, $p = 0.0435$). The UPL symbol represents upland runoff data from collectors located in the S2 Watershed and were not used in the regression.

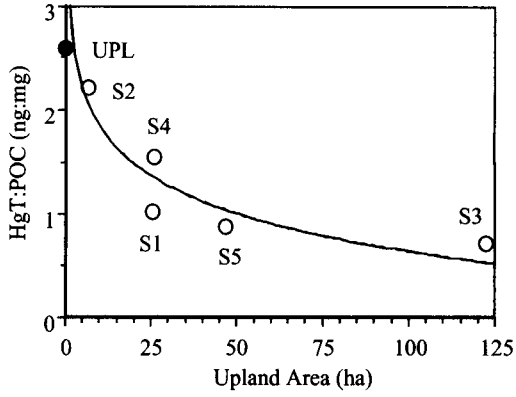

Fig. 5. Relationship between upland area and the HgT/POC ratio for watershed outlet waters at the Marcell Experimental Forest (HgT = 3.04 − 1.20(Log Upland Area), $r^2 = 0.84$, $p = 0.0219$). The UPL symbol represents upland runoff data from collectors located in the S2 Watershed, and were not used in the regression.

Table 2. Annual and mean fluxes of HgT and OC for the five study watersheds (standard error in parentheses).

Watershed	Year	Flow	HgT	DOC	POC
		cm	mg	kg	
S1	1993	9.6	189.5	1661	198.3
	1994	11.6	336.4	1730	245.8
	1995	11.0	166.3	1616	117.1
Mean		10.7 (1.0)	230.7 (56.2)	1669 (132)	187.1 (40.4)
S2	1993	16.8	265.7	901.1	123.6
	1994	20.2	339.1	1011.8	110.3
	1995	19.2	218.2	981.0	98.9
Mean		18.7 (1.0)	274.2 (35.4)	964.6 (35.4)	110.9 (7.3)
S3	1994	131.5	3215	7105	2186
	1995	124.0	1953	7922	1701
Mean		127.8 (9.8)	2584 (678)	7514 (804)	1944 (303)
S4	1993	21.5	661.1	3763	417.1
	1994	25.2	771.8	3690	404.0
	1995	24.0	820.5	3487	337.0
Mean		23.6 (2.0)	751.1 (114.4)	3647 (506)	386.0 (58.4)
S5	1993	11.7	1056	3164	573.6
	1994	13.6	921	3390	430.4
	1995	13.0	1289	3132	553.0
Mean		12.8 (1.4)	1089 (152)	3229 (326)	519.0 (68.4)

of propagation of uncertainty associated with concentration measurements, predicted flow and the variation among the 3 yr of the study (2 yr for the S3 Watershed).

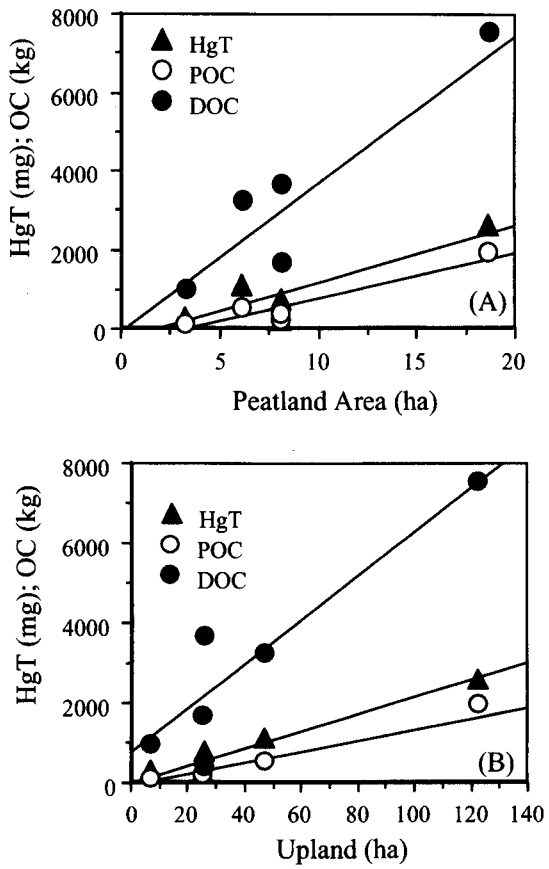

Fig. 6. Relationships between total outlet fluxes of HgT, POC, and DOC and (*A*) peatland (HgT = −319 + 148(Peatland Area), r^2 = 0.80, p = 0.0398; POC = −448 + 122(Peatland Area), r^2 = 0.89, p = 0.0152; DOC = −202 + 409(Peatland Area), r^2 = 0.87, p = 0.0200) and (*B*) upland area (HgT = 44.6 + 20.7(Upland Area), r^2 = 0.96, p = 0.0038; POC = −114 + 16.4(Upland Area), r^2 = 0.98, p = 0.0016; DOC = 971 + 53.6(Upland Area), r^2 = 0.92, p = 0.0144) for watersheds at the Marcell Experimental Forest.

Standard errors associated with S2 are smaller because flow was directly measured.

Mean annual HgT and OC fluxes were related to both upland area and peatland area (Fig. 6). Multiple regressions were developed to separate the fluxes between upland and peatland areas. Dependent variables were annual watershed fluxes of HgT, DOC, and POC, and independent variables were areas of upland and peatland in each watershed; regressions were forced through zero (Table 3). Peatland fluxes dominate the transport of HgT, DOC, and POC in all watersheds with upland fluxes becoming more important in watersheds with higher upland/peatland ratios, such as S3 and S5 (Table 4). Based on the equations (Table 3), peatlands play a more significant role in transport of DOC than HgT or POC (Table 4). This emphasizes our earlier point that peatland area was more closely related to the HgT associated with DOC while upland area was more closely related to the HgT/POC ratio.

Although total fluxes of HgT and OC are related to areas of peatland and upland, comparisons are compromised because of correlations of area with flow, especially peatland area (r^2 = 0.97, p = 0.0027). To avoid these problems, total fluxes were converted to fluxes per unit area of watershed (Table 5). Although the groundwater driven fen (S3) has significantly higher flow per unit area, fluxes of HgT and DOC are within the range of the runoff driven bog watersheds (Table 5). The lower concentrations present in fen waters compensate for the higher flow, producing similar fluxes of HgT and DOC per unit area. The S3 fen does have the highest fluxes of POC per unit area of the watersheds studied (Table 5). With higher fluxes of POC but similar fluxes of HgT as the bog watersheds, less HgT is associated with POC in the fen. The range of HgT export from streams at the Marcell Experimental Forest falls within the range reported in the literature (0.2–4.4 μg m^{-2} yr^{-1}, Mierle, 1990; 1.5–1.8 μg m^{-2} yr^{-1}, Lee et al., 1995; 1.2–2.1 μg m^{-2} yr^{-1}, St. Louis et al., 1994).

Watershed fluxes of DOC per unit area are not re-

Table 3. Multiple regression equations developed to predict annual HgT, DOC, and POC fluxes (PLA = peatland area in ha, UPA = upland area in ha, $n = 5$). Peatland area and upland area are not significantly related ($p > 0.05$). Regression coefficients are all significant at the 0.10 confidence level and models are all significant at the 0.01 confidence level.

Flux	Regression model	PLA (p)	UPA^2 (p)	r^2
HgT	HgT (mg) = (68 × PLA) + (0.10 UPA^2)	0.12	0.15	0.89
DOC	DOC (kg) = (340 × PLA) + (0.09 UPA^2)	0.03	0.58	0.89
POC	POC (kg) = (32 × PLA) + (0.09 UPA^2)	0.05	0.01	0.98

Table 4. Percentages of HgT, DOC, and POC fluxes from the upland and peatland portions of the watersheds studied, based on equations in Table 3.

	HgT		DOC		POC	
Watershed	% Peatland	% Upland	% Peatland	% Upland	% Peatland	% Upland
S1	90	10	92	2	81	19
S2	98	2	99	1	96	4
S3	82	18	96	4	69	31
S4	89	11	98	2	80	20
S5	67	33	92	8	49	51

lated to HgT fluxes among watersheds; however, POC and HgT fluxes are related, but only for the bog watersheds (Fig. 7). These results suggest that transport of HgT by DOC is independent of peatland type, while transport of HgT associated with POC is influenced by peatland type present in the watershed.

DISCUSSION

Total Mercury and Organic Carbon Concentrations

The processes controlling the transport of HgT from the watersheds at the Marcell Experimental Forest are complex. It is clear that both DOC and POC influence transport of HgT from the upland and peatland portions of the watershed. The two OC fractions were not related to one another. The S3 fen watershed had the highest correlation, ($r^2 = 0.36$, $p > 0.1$) while those of the bog watersheds were lower or even negative in some cases. We therefore do not believe that covariance is a problem in our interpretations.

While relationships between HgT and OC concentrations exist for individual watersheds, the relationships are stronger for POC than for DOC. It appears that POC is the most important terrestrial transport mechanism for total HgT, although the HgT/POC ratio depends on the watershed. The proportional extent of uplands and peatlands best account for variations in HgT/OC concentrations among watersheds. The results suggest that peatlands are more influential in establishing the relationship between HgT and DOC (Fig. 4) while the uplands control the HgT/POC ratio in stream waters (Fig. 5). Previous forest management practices on the watersheds do not appear to significantly influence these relationships.

Driscoll et al. (1994) found that the percent of nearshore wetlands in the drainage basin of 16 Adirondack lakes explained 65% of the variability in total HgT concentration in the lakes. We found that peatland area accounts for 94% of the variability in mean volume weighted total HgT concentration (Fig. 8). Our results and those of Driscoll et al. (1994) suggest that watershed parameters related to wetland extent show promise in predicting HgT concentrations in surface waters.

Total Mercury and Organic Carbon Fluxes

Fen peatlands have fundamentally different hydrologic and chemical regimes than do bogs (Boelter and Verry, 1977). Fluxes of HgT associated with DOC behave similarly among all watersheds, but fluxes of HgT associated with POC behave differently in the watershed with a fen (Fig. 7). Less HgT is associated with the POC transported through the fen watershed than in the bog watersheds. We hypothesize that water residence time is an important factor leading to the lower HgT/POC ratio in fen-derived stream waters. Because S3 has the largest watershed and peatland, the mean residence time of waters flowing through the system are likely greater than those of the bog watersheds. As discussed earlier, POC transport in streams may increase with watershed size, but the proportion of HgT in the load decreases because of the greater opportunity for HgT to volatilize (Lindberg et al., 1995) or be complexed with more immobile forms of soil OC.

It is apparent that the suspended particulate fraction of mobile organic C plays an important role in HgT transport. By using the relationships in Fig. 3 and the mean annual volume weighted concentrations for HgT, DOC, and POC, the percentage of HgT transported

Table 5. Unit area flux of HgT and OC from watersheds in the Marcell Experimental Forest (standard errors in parentheses).

Watershed	Area	Flow	HgT flux	TOC flux	DOC flux	POC flux
	ha	kL m^{-2}	μg m^{-2} yr^{-1}	g m^{-2} yr^{-1}		
S1	33.2	0.11 (0.01)	0.70 (0.17)	5.60 (0.48)	5.06 (0.40)	0.57 (0.12)
S2	9.7	0.19 (0.01)	2.82 (0.36)	11.06 (0.33)	9.92 (0.36)	1.14 (0.07)
S3	140.0	0.66 (0.05)	1.88 (0.49)	6.87 (0.64)	5.46 (0.59)	1.41 (0.22)
S4	34.0	0.24 (0.02)	2.15 (0.33)	11.53 (1.61)	10.42 (1.44)	1.10 (0.17)
S5	52.6	0.13 (0.01)	1.85 (0.26)	6.35 (0.62)	5.47 (0.55)	0.88 (0.12)

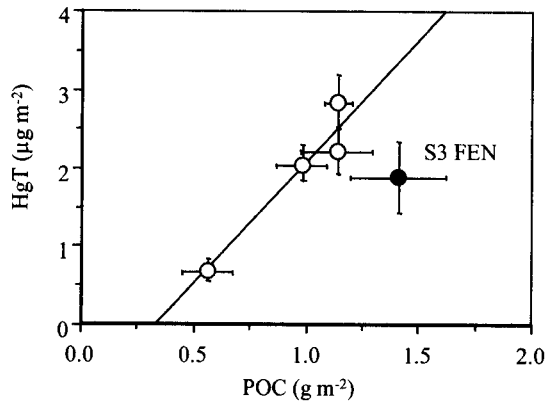

Fig. 7. Relationship between annual unit area fluxes of HgT and POC for watersheds at the Marcell Experimental Forest (fen not included the relationship, HgT = −1.08 + 3.17(POC), r^2 = 0.93, p = 0.0376).

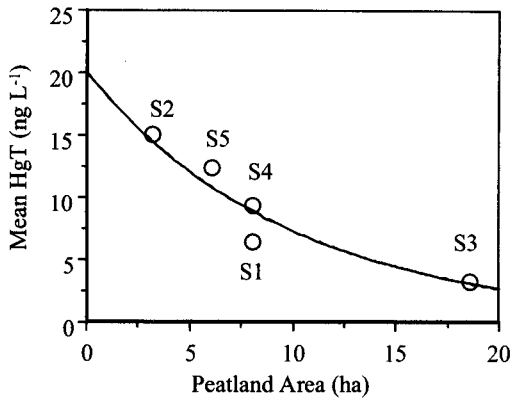

Fig. 8. Relationship between mean volume weighted HgT concentration and peatland area for watersheds at the Marcell Experimental Forest (HgT = 20.0 × 10 $^{(-0.044 \times \text{Peatland Area})}$, r^2 = 0.94, p = 0.0106).

by each OC fraction can be estimated (Table 6). The percentage of HgT transported by POC ranges from 52 to 80% for the watersheds at the Marcell Experimental Forest even though POC only contributes approximately 10 to 15% of the OC fluxes for the bogs and 25% for the fen.

CONCLUSION

Both the dissolved and particulate organic fraction are important transport mechanisms of HgT. Although this study was designed to investigate the role of TOC in HgT transport, the results suggest that POC is the dominant vector of transport in all five watersheds. Variations in upland and peatland forest canopy and differences in past forest management among watersheds do not appear to strongly affect the relationships between HgT and OC fluxes. Instead, the hydrology as it relates to watershed geometry (the extent of upland and peatland in the watershed) and water sources, have the greatest effect on HgT and OC fluxes. These findings have important implications for forest management if HgT transport from terrestrial systems to surface waters is to be reduced. Silvicultural or construction practices that generate particulates, especially upland particulates, should be avoided or controlled. Design strategies

Table 6. Mean annual volume weighted HgT, DOC, and POC concentrations and the percentage of HgT transport associated with each organic fraction.

Watershed	HgT	DOC	POC	DOC %	POC %
	ng L^{-1}	mg L^{-1}			
S1	6.45	47.38	5.30	30.9	69.1
S2	15.06	53.04	6.16	30.4	69.6
S3	3.21	9.49	2.39	25.5	74.5
S4	9.37	45.79	4.85	20.4	79.6
S5	12.43	36.76	5.96	47.9	52.1

that lessen particulate transport to surface waters and wetlands, such as the use of buffer strips, should be encouraged. Considering that the terrestrial transport of HgT can account for up to 62% of the HgT present in drainage lakes (Henning et al., 1989), and that HgT associated with the particulate organic fraction can contribute up to 80% of the total watershed flux, up to 50% of the HgT in drainage lakes could be derived from terrestrial particulates.

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