

MERCURY IN SOIL, SOIL WATER, AND STREAM WATER IN TWO FORESTED CATCHMENTS ON MT. MANSFIELD, VERMONT

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ABSTRACT. Soil solution and stream water from locations in two small forested catchments in Underhill Center, VT were collected April–November 1997 and analyzed for mercury (Hg), dissolved organic carbon (DOC), color, trace elements, and major ions. Mercury concentrations in Oa and B horizon soil water ranged from 1.1 to 34.9 ng L⁻¹ and 0.1 to 10.2 ng L⁻¹, respectively. In streams, dissolved Hg was 0.9 to 4.1 ng L⁻¹ and total (dissolved + particulate) Hg was 0.9 to 9.2 ng L⁻¹. Mercury and other trace metals were typically present in higher concentrations in soil water than streams, indicating additional removal of these elements below the sampling depths before reaching streams. In soil water and stream water, Hg was positively correlated with DOC and color. Mercury concentrations followed a pattern similar to other trace metals that form complexes with organic compounds, such as Al, Cr, Cu, and Pb. Most of the Hg in the streams is associated with particulate matter, but the small and continual contribution of dissolved Hg from soil water and groundwater also exports significant amounts of Hg from these forested systems.

This report includes the main findings of my master's thesis. Copies of the thesis (with the complete data set included in appendices) are on file at the University of Vermont library and at the VForEM headquarters.

INTRODUCTION

Mercury (Hg) contamination in freshwater fish is a widespread environmental problem throughout the northern hemisphere. Atmospheric sources of Hg are thought to be responsible for increasing Hg burdens in Lake Champlain (Watzin, 1992; Scherbatskoy *et al.*, 1997) but the sources and mechanisms of transport and accumulation are not well understood. Because of the large land-to-lake area ratio of the Lake Champlain basin (19:1), with 64% of the land area forested (unpublished data, Vermont Center for Geographic Information, October 1998), the presence of Hg in forest soils likely influences the loading of Hg to the surface waters that drain into Lake Champlain.

Mercury in forest soils is strongly bound to soil constituents or revolatilized into the atmosphere. In a small forested catchment in Underhill Center, VT, dissolved Hg concentrations in stream water are consistently low (< 4 ng L⁻¹), but accounted for 26 and 38% of the total Hg exported in the stream during two years of study (Scherbatskoy *et al.*, 1998). Although Hg has also been shown to be primarily associated with suspended sediment in rivers and streams (Kolka, 1996; Balogh *et al.*, 1997; Scherbatskoy *et al.*, 1998), the small percentage of Hg mobilized from soils to streams may contribute 25–75% of Hg reaching lakes (Lee *et al.*, 1994).

The objectives of this work were to: (i) determine the concentrations of Hg, dissolved organic carbon (DOC), and several trace metals in soil and stream solutions in two small catchments in the Lake Champlain basin, (ii) compare the behavior of Hg with DOC and trace metals in these media, and (iii) use the results to identify factors that might affect the transport of dissolved Hg in an upland catchment.

MATERIALS AND METHODS

SITE CHARACTERISTICS

This study focuses on two small catchments on the western slope of Mt. Mansfield in Underhill Center, VT (Figure 1). The sites are centrally located in the Lake Champlain basin, approximately 31 km northeast of Burlington, VT and 120 km south-southeast of Montréal, PQ. Both sites lie within the Lamoille River watershed. Nettle Brook is a small stream draining an 11-ha mixed hardwoods catchment between 445 and 664 m elevation. Since October 1993, water samples have been collected for Hg and major ions at a continuously gauged v-notch weir at 445 m elevation. Stream 10 is a small stream draining a 7.4-ha mixed conifer and hardwoods catchment between 775 and 1180 m elevation. Water samples have been collected here since March 1995.

FIELD SAMPLING TECHNIQUES

Passive capillary wick soil water samplers were custom made based on designs described in Holder *et al.* (1991); Knutson *et al.* (1993); and Knutson and Selker (1996), and shown in Donlon (1999). Two shallow collectors (just below the Oa horizon, 4–7 cm below ground surface) and two deep collectors (below the Bhs or within the B horizon, 22–28 cm below ground surface) were installed at each of two sampling locations along Nettle Brook (Middle and Upper sites shown on Figure 1). At the Stream 10 site, it was only possible to install one lysimeter at each depth because of rock obstructions and seasonal time constraints. A total of 10 lysimeters were installed between 26 September and 18 December 1996.

Soil solution and stream samples were collected during spring snowmelt and major rain events between 20 April and 3 November 1997. Bottles for collecting soil solution were set out just prior to each storm event and were collected when the bottle was full or after precipitation ended. Grab samples of stream water were collected during storms near the three soil water sites and at the Nettle Brook weir (Figure 1), with an attempt to collect successive samples during the storm as stream flow increased, crested, and descended. Typically it was only possible to sample once before and once after stream flow peaked.

Soil samples were also collected in December 1997 at each soil water sampling site within a 10 m vicinity of the lysimeters. Soil samples were collected at two depths (4–7 cm and 22–28 cm, or the same horizons where the lysimeters were placed) using a soil corer. Soil that did not come in contact with the corer was collected into acid-cleaned polypropylene vials.

Clean technique was used in handling all samples: all equipment and supplies used in sampling were rigorously acid-cleaned in a 4 or 11 day cycle (Burke *et al.*, 1995); sample bottles were Teflon-taped and triple-bagged; and particle-free gloves were worn when handling the samples.

SAMPLE PROCESSING

Upon collection, samples were brought to Proctor Maple Research Center (PMRC) in Underhill Center, VT. Subsamples were poured off inside a portable counter-top HEPA-filtered clean chamber for analysis of pH, conductivity, DOC, color, and major ions. Samples for Hg and trace metals analyses were

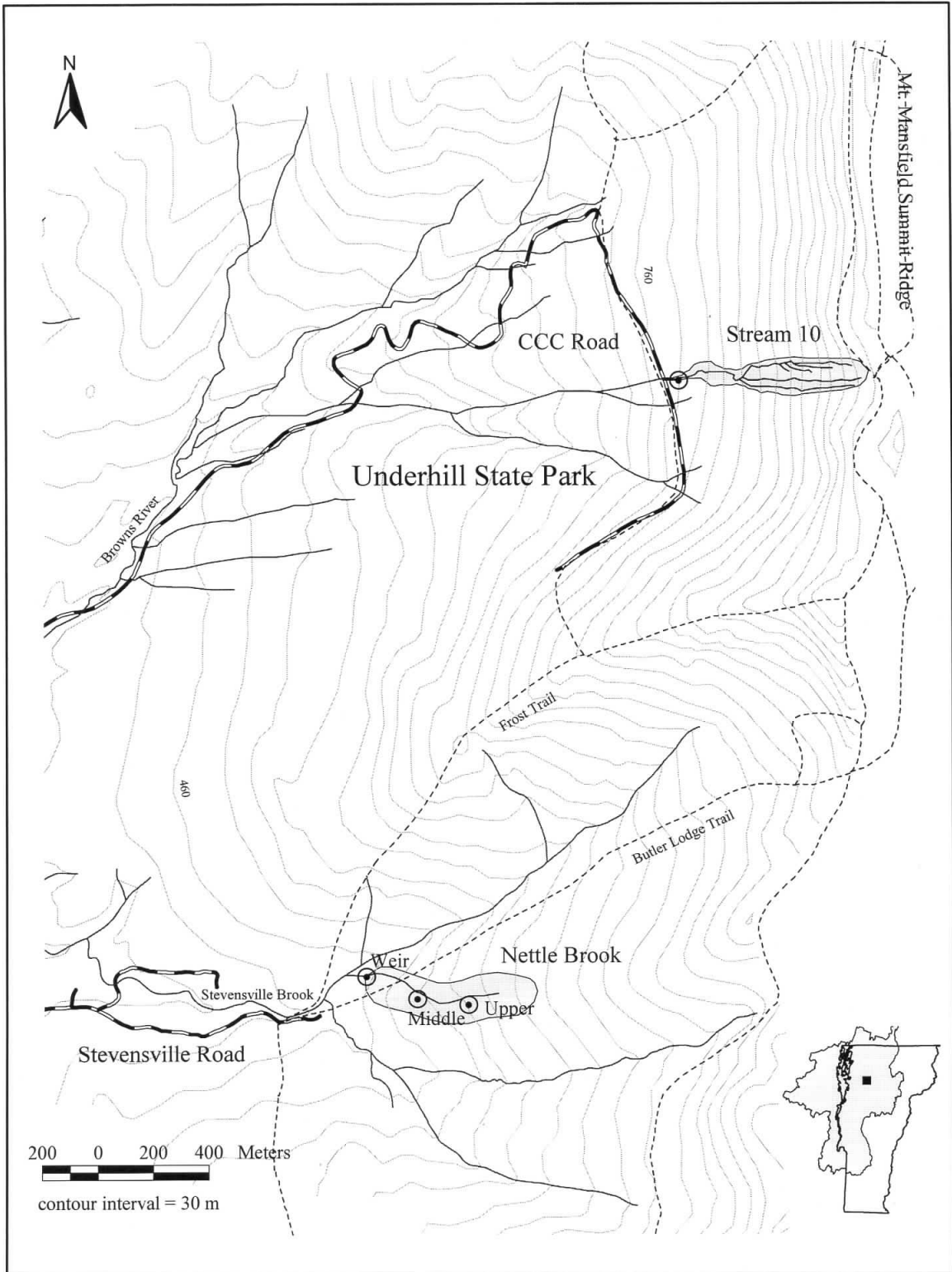


Figure 1. Site map. Circles indicate soil water and stream sampling locations. Inset shows the location of the study sites within the boundaries of Vermont and the Lake Champlain basin.

shipped by overnight courier to the University of Michigan Air Quality Laboratory (UMAQL) in Ann Arbor, MI where they were oxidized with BrCl to a 1% solution and refrigerated until analysis. Subsamples of those samples with sufficient volume were filtered before oxidation through 0.22- μ m nitrocellulose filters (Millipore MF) to separate operationally-defined dissolved and particulate fractions. This size filter was chosen to maximize discrimination between dissolved Hg and Hg associated with particles.

Subsamples retained at PMRC were analyzed for pH (Orion EA920) and conductivity (VWR Scientific EC 2052), and then filtered using a 0.7- μ m glass fiber syringe filter (Whatman 13-mm ZC GF/F). This size filter was chosen because it is the smallest glass fiber syringe filter available. Filtered water samples were refrigerated until analysis for DOC, color, and major ions.

Soil samples were shipped to UMAQL where they were dried, ground with acid-cleaned glass mortars and pestles, and microwave digested with 10% HNO₃ as described in Rea and Keeler (1998).

LABORATORY ANALYSIS

All Hg analysis was performed at the UMAQL in a Class 100 clean room using cold vapor atomic fluorescence spectrometry (CVAFS). Trace metal analysis at UMAQL was conducted on a Perkin-Elmer Elan 5000A inductively coupled plasma-mass spectrometer (ICP-MS) equipped with a thin film electron multiplier. The elements that were analyzed on this machine include Li, Be, Mg, Al, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Ba, La, Ce, Nd, Sm, Tl, and Pb. The full set of analytical results is presented in Donlon (1999).

DOC was determined by ultraviolet persulfate oxidation with infrared detection at the USGS laboratory in Albany, New York using a Dohrman C analyzer. Color was analyzed on a UV-visible recording spectrophotometer (Shimadzu UV160U) at the University of Vermont School of Natural Resources. Absorbance at 420 nm was compared against a standard curve using platinum cobalt (Pt Co) solutions (Fischer SP120-500) (Black and Christman, 1963).

Major elements and ions (Ca, K, Mg, Na, S, Si, P, NH₄⁺, Cl⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻) were analyzed following standard methods at the University of Vermont Agricultural and Environmental Testing Laboratory. A Perkin-Elmer Optima DV inductively coupled plasma atomic emission spectrophotometer (ICP-AES) was used to measure concentrations of elements. Nitrate and ammonium were determined by colorimetric analysis on a Lachat QuikChem AE flow injection analyzer. Chloride, phosphate, and sulfate were measured by chemically suppressed ion chromatography using a Dionex 2000 series instrument. In addition to the water samples, soil samples collected from the study sites were analyzed for C, H, and N. These samples were analyzed using an Exeter Analytical CE440 CHN elemental analyzer.

RESULTS

SOILS

Two soil samples were collected at two depths at each of the three study sites. Results from two samples (Oa depth at the Upper Nettle and Stream 10 sites) are not available because of possible contamination in one of the samples and laboratory error in the other. Because of the small number of

samples collected, the data give only a general idea of the level of Hg in soils at the sites. The average Hg concentrations at the Oa horizon (4–7 cm below ground surface) were 151.0, 309.4, and 169.0 ng g⁻¹ (dry weight) at mid Nettle, upper Nettle, and Stream 10, respectively. Oa soils at these sites contained 11–18% carbon. The average Hg concentrations at the B horizon (22–28 cm below ground surface) were 68.9, 46.6, and 74.7 ng g⁻¹ (dry weight) at the three sites, respectively. B horizon soils at these sites contained 1.4–3.7% carbon. Figure 2 presents Hg and DOC concentrations in soil, soil water, and stream water by site.

At all sites, Hg concentrations in soil were higher in the Oa horizon than in the B horizon. Other trace metals that followed this trend include As, Ba, Cd, and Pb. Several other trace metals followed the opposite trend, with higher concentrations in the B horizon, including Al, Ce, Cr, La, Mg, Mn, Ni, and Zn.

SOIL WATER

Soil water was collected during one spring snowmelt event and eight summer and fall rainstorms between 20 April and 3 November 1997 at the Nettle Brook sites, and during six summer and fall rainstorms at the Stream 10 site. Concentrations of Hg were significantly higher in Oa horizon soil water than in B horizon water at all three sites. DOC and color were also higher in the Oa horizon soil water, but significance varied by site. Mercury, DOC, and color was significantly lower at the upper Nettle site than the other sites at both depths. The upper Nettle site is located on a wet hillslope.

Soil water pH at all sites was lower in the Oa horizon, but the difference was only statistically significant at the mid Nettle site. Soil water pH at the Stream 10 site was significantly lower than the Nettle sites at both depths. Stream 10 is the site at highest elevation.

Mercury in Oa horizon soil water was positively correlated with DOC and color at all three sites ($r^2 = .81-.98$, $p = .03-.0002$ at individual sites). In B horizon water, the positive correlation between Hg and DOC or color was not as strong but sample sizes were smaller. Hg in soil water was most consistently correlated with DOC and color but also tended to be positively correlated with As, Cu, Pb, Ti, and rare earth metals (Ce, La, Sm), and negatively correlated with K, Na, Rb, and NO₃.

Most trace metals followed the pattern of higher concentrations in Oa horizon soil water than in B horizon water. However, no trace metals were analyzed in B horizon water at the mid Nettle site because of insufficient sample volumes collected at this depth. At the Stream 10 site, several trace metals and ions followed the opposite trend and were present in higher concentrations in B horizon soil waters, including Ca, Cr, Mg, Mn, Na, Si, SO₄, and Zn.

STREAM WATER

Stream samples were collected near the three soil water sampling sites and at the Nettle Brook weir during rain events when soil water was collected. There were no statistically significant differences in the total Hg, dissolved Hg, and DOC concentrations between sites. Color at the upper Nettle location was significantly higher than at Stream 10 ($F = 4.25$, $p = .0096$). The upper Nettle site is directly downstream from a boggy area. Stream pH was significantly higher at the lowest elevation site (Nettle weir) and significantly lower at the highest elevation site (Stream 10) ($F = 335.47$, $p = .0001$).

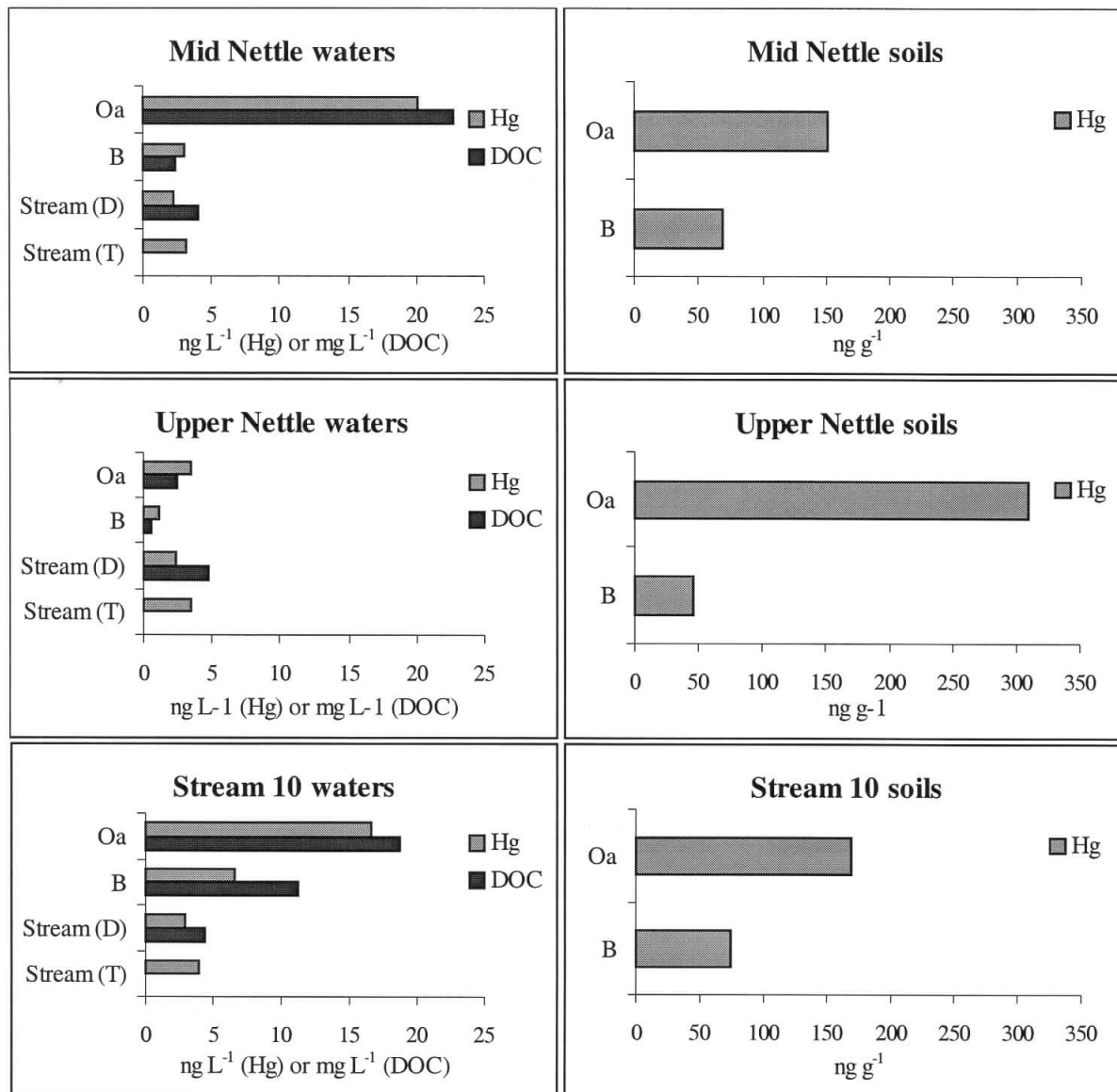


Figure 2. Mercury and DOC concentrations in soil water, stream water, and soils collected between April and November, 1997 in Underhill Center, VT.

Total and dissolved Hg were positively correlated with DOC and color at all sites ($r^2 = .51-.96$, $p = .09-.001$ for each site). Total and dissolved Hg were also positively correlated with Al, As, Cu, Cr, Ni, Pb, Ti, V, rare earth metals (Ce, La, Nd, Sm), and stream temperature. Mercury tended to be negatively correlated with Cl, Na, and SO_4 .

Concentrations of most analytes were higher in soil water than in stream water. Exceptions to this trend occurred at Stream 10 (for Cu, La, Mn, Ce) and at the upper Nettle site (for As, Ba, Mn), where stream concentrations of these elements exceeded soil water concentrations by 6 to 60%. Mercury and V in stream water were roughly equal to that of soil water at the upper Nettle site. The upper Nettle site is on a wet hillslope with many seeps.

At the Nettle weir, where flow rate was continually measured, total Hg (particulate + dissolved) and most other trace metal concentrations increased as flow increased. Dissolved Hg concentrations, on the other hand, only slightly increased as flow increased. This was also true for Cu, but dissolved Al, Nd, and Pb increased as flow increased. Concentrations of dissolved Ca, Mg, Si, and SO_4 became diluted as flow increased, which is a typical pattern for groundwater-derived chemicals. At lower flow conditions, Hg had a higher dissolved proportion than most trace metals but as flow increased, more and more Hg was associated with particles. Although other trace metals such as Al, Cu, Ce, and Pb also followed this pattern, it is notable that Hg and Ti (a crustal element) show the strongest decrease with flow.

DISCUSSION

In soils, Hg had higher concentrations in the Oa horizon than in the B horizon, as did As, Ba, Cd, and Pb. These elements have atmospheric sources, and their prevalence in the Oa horizon probably reflects accumulation resulting from atmospheric deposition, as byproducts from fuel combustion, metal smelting, and other uses (Nriagu and Pacyna, 1988). Barium has recently been proposed to be a good indicator of unleaded gasoline and diesel oil emissions (Monaci and Bargagli, 1997). The elements Al, Ce, Cr, La, Mg, Mn, Ni, and Zn, had higher concentrations in the B horizon. These elements have a crustal origin, and are likely present as products of bedrock weathering, although Cr, Mn, Ni, and Zn can also have atmospheric sources (Driscoll *et al.*, 1988; Nriagu and Pacyna, 1988).

Soils are a net sink for atmospherically deposited Hg. Using the Hg input–output balance at Nettle Brook presented by Scherbatskoy *et al.* (1998) and a re-volatilization rate of $90 \text{ mg ha}^{-1} \text{ yr}^{-1}$ (in Sweden; Bishop *et al.*, 1998), it is likely that Hg is accumulating in catchment soils.

The observed pattern of higher Hg (or other trace metals) and DOC in Oa horizon soil water than B horizon soil water has been noted in part by others (McDowell and Wood, 1984; Bergkvist, 1987; Driscoll *et al.*, 1988; Lazerte *et al.*, 1989; David *et al.*, 1992; Bishop *et al.*, 1995). These analytes also tended to have higher soil water concentrations than stream water concentrations, indicating that additional adsorption of these ions and metals occurs as water percolates downward and discharges into the streams as groundwater. Removal of DOC and trace metals in the upper part of the B horizon is a part of natural soil formation (Bergkvist, 1987; Cantrell, 1989). The relatively high Hg concentrations that were found in Oa horizon soil water represents Hg that will largely be retained in the catchment, attached to soil or re-volatilized to the atmosphere.

At the Nettle Brook weir, flow-related increases in total stream water concentrations of Hg and also Li, Al, Ti, Mn, Co, Cu, Zn, Cd, La, Ce, Nd, Sm, and Pb were observed during the study. The majority of Hg transport occurs during the highest flow events, particularly during years of significant and rapid snowmelt (Scherbatskoy *et al.*, 1998). Release of Hg in rivers and stream water during increased flow events has been shown to be related to sediment transport (Balogh *et al.*, 1997; Scherbatskoy *et al.*, 1998). Dissolved stream water concentrations at the Nettle Brook weir were not as sensitive to stream flow rate as the total (dissolved + particulate) concentrations were. As observed in previous years of study (Scherbatskoy *et al.*, 1998), dissolved Hg concentrations only slightly increased with increased flow. The pattern of Hg as a function of stream flow points towards stream flow rates and the amount of suspended sediment as being critical to the behavior of Hg.

Based on the concentrations of Hg we observed in Oa soils and soil water, an event that causes a rise in the water table high enough to direct flow from the upper soil horizons to streams should cause more Hg and DOC to be exported to streams. However, we have never observed a dramatic increase in dissolved Hg at Nettle Brook. Instead, dissolved Hg represents a small but steady input to Nettle Brook. Why doesn't dissolved Hg seem to behave like DOC or dissolved Al, Zn, Cd, or Pb at Nettle Brook, which do increase with increased flow? It is possible that dissolved Hg coming from soil water or other sources during storms is quickly adsorbed by suspended organic particulate matter upon entry into the stream. Adsorption could occur immediately or in the sample bottle before analysis. The order of affinity to organic compounds ($\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} = \text{Cd}^{2+} > \text{Mn}^{2+}$) (Cheam and Gamble, 1974; Förstner and Wittman, 1981; Takamatsu *et al.*, 1983) might support these hypotheses, especially because dissolved Cu also did not increase much with flow. Mercury's relationship with reduced S functional groups on organic compounds (Xia *et al.*, 1999) might make adsorption onto suspended sediment more favorable for Hg-organic complexes than for complexes with other metals in uncontaminated waters.

Given that Hg is primarily exported in association with particulate matter in forest streams, land use practices that minimize soil erosion into streams (such as during logging) will also serve to limit transport of Hg to surface waters and ultimately to Lake Champlain. The fate of this Hg as it travels downstream towards Lake Champlain through agricultural and developed lands has not yet been explored. Much of the particulate phase Hg in upland watersheds may be re-deposited further downstream. Ultimately the Hg present in dissolved form may be enough to account for the Hg entering the food web in Lake Champlain, but no research has yet been done to look at the cycling of Hg in this lake and its watershed.

ACKNOWLEDGMENTS

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