

Hydrologic Cycling of Mercury and Organic Carbon in a Forested Upland–Bog Watershed

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ABSTRACT

The hydrologic cycling of total Hg (HgT) and organic C (OC) was studied for a 1-yr period in a northern Minnesota forested watershed, consisting of an upland surrounding a bog peatland with a narrow lag at their interface. Throughfall and stemflow contributed twice as much HgT and seven times as much OC to the forested watershed than atmospheric deposition in a nearby opening. Fluxes in upland runoff accounted for 16% of the HgT and 8% of the OC inputs to the lag and were dominated by interflow transport. Bog runoff accounted for 57% of the HgT and 83% of the OC inputs to the lag. For an annual cycle, upland soils were sinks for both HgT and OC, while bog soils were sinks for HgT but sources of OC. Fluxes to the lag accounted for 184% of the HgT and 87% of the OC transported from the watershed outlet. We speculate that HgT was lost in the lag by both volatilization and soil accumulation. Total Hg and dissolved organic C (DOC) are positively related in both throughfall and stemflow, with stemflow showing the strongest relationships. In the soil system, HgT–DOC relationships deteriorate and HgT–particulate organic C (POC) relationships dominate. Water residence time in contact with OC appears to be important in determining the relationships between HgT and OC. At the stream outlet, our data suggest that ≈70% of the HgT transported from the watershed is associated with POC, while 30% is associated with DOC.

THE HYDROLOGIC TRANSPORT of HgT through terrestrial environments to surface waters is little studied and poorly understood, even though terrestrial transport is widely acknowledged to be important in determining the ultimate fate of atmospherically deposited HgT with respect to the aquatic environment (Lindqvist, 1991). The majority of atmospheric HgT deposition in a typical forested watershed occurs on terrestrial landscapes because of (i) the greater proportion of land relative to surface water and (ii) the higher rate of dry deposition associated with tree canopies (Kolka et al., 1999a). Studies in Minnesota and adjacent areas indicated that 25% of the atmospheric HgT deposited on terrestrial basins reaches associated lakes (Swain et al., 1992). These data demonstrated the importance of determining the loadings of HgT from terrestrial to aquatic components of watersheds.

Studies that have emphasized HgT in terrestrial environments have investigated individual processes of dry deposition (Iverfeldt, 1991; Lamborg et al., 1994; Kolka et al., 1999a), throughfall (Iverfeldt, 1991; Lindberg et al., 1994; Munthe et al., 1995; Kolka et al., 1999a), stemflow (Kolka et al., 1999a), and stomatal uptake (Lindberg et al., 1991; Hanson et al., 1995). Others have ad-

ressed regional-scale (Steinnes and Andersson, 1991; Johansson et al., 1991; Nater and Grigal, 1992) or global questions (Fitzgerald, 1986; Hudson et al., 1995) or have emphasized HgT pools rather than transport (Grigal et al., 1994; Lee et al., 1994).

It is well known that HgT forms strong complexes with organics (Kabata-Pendias and Pendias, 1992). Although not well characterized, OC in wetlands appears to influence the hydrological flux of HgT (Driscoll et al., 1994; Kolka et al., 1999b). Total Hg is positively correlated with OC in soil solution (Aastrup et al., 1991), stream and runoff waters (Lee and Iverfeldt, 1991; Johansson et al., 1991; Johansson and Iverfeldt, 1994; Hurley et al., 1995; Kolka et al., 1999b), and in lake waters (Sorensen et al., 1990; Meili et al., 1991; Lee and Iverfeldt, 1991; Driscoll et al., 1994, 1995). If a close relationship exists between HgT and OC in solutions within and among hydrologic compartments, and if that relationship is verified and quantified, then the prediction of sites and processes associated with enhanced HgT transport will become attainable.

To develop land management strategies to minimize the transport of HgT to aquatic environments, knowledge at the landscape or watershed scale is necessary. Total Hg mass balance studies have investigated atmospheric inputs and terrestrial outputs to lakes (St. Louis et al., 1994; Hultberg et al., 1994; Krabbenhoft et al., 1995), but few have studied HgT cycling in peatland watersheds (Branfireun et al., 1996; St. Louis et al., 1996), and no studies have monitored both upland and peatland hydrologic components and related HgT transport to OC transport. Our objectives were to develop a hydrologic mass balance of the HgT and OC in an upland–peatland watershed and to investigate the relationships between HgT and OC in those waters of the hydrologic cycle (Fig. 1). This study addresses some of the existing gaps in the knowledge regarding the terrestrial transport of HgT and provides an integrated, watershed-scale view of the major hydrologic fluxes responsible for transport of HgT from terrestrial to aquatic environments.

MATERIALS AND METHODS

Study Site

The S2 watershed is located on the USDA Forest Service Marcell Experimental Forest, located 40 km north of Grand Rapids, MN (47°32'N, 93°28'W) (Fig. 2). The S2 watershed contains a 3.0 ha-bog and a 6.2-ha upland. The stream pH at the watershed outlet is 3.9 ± 0.2 ($n = 48$, 1993–1995). Bog

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Abbreviations: DOC, dissolved organic C; HgT, total mercury; NADP, National Atmospheric Deposition Program; OC, organic C; PHIM, Peatland Hydrologic Impact Model; POC, particulate organic C; PVC, polyvinyl chloride; SE, standard error; TOC, total organic C.

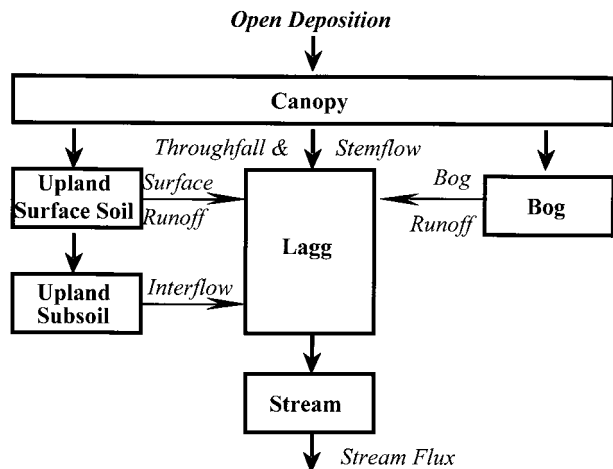


Fig. 1. Mass balance model of the hydrological components of an upland-peatland watershed.

vegetation consists of an overstory of black spruce [*Picea mariana* (Mill.) B.S.P.] with an understory of ericaceous shrubs including Labrador tea (*Ledum groenlandicum* Oeder), leatherleaf [*Chamaedaphne calyculata* (L.) Moench.], and bog rosemary [*Andromeda polifolia* L. var. *glaucophylla* (Link) DC], with a mat of sphagnum moss (*Sphagnum* spp.) and sparse herbaceous cover. Upland vegetation in S2 is primarily composed of trembling aspen (*Populus tremuloides* Michx.), bigtooth aspen (*P. grandidentata* Michx.), and paper birch (*Betula papyrifera* Marsh.), with an understory of beaked hazel (*Corylus cornuta* Marshall), American hazel (*C. americana* Walter), bracken fern [*Pteridium aquilinum* (L.) Kuhn], and herbs. Flow from the nutrient-rich upland and nutrient-poor domed bog meet at the bog margin, creating a narrow hydrologically active area around the circumference of the peatland. This small area, known as the lagg, is the source of flow at the outlet. Vegetation in the lagg consists of speckled alder [*Alnus rugosa* (Du Roi) Spreng.], willow (*Salix* spp.), and tamarack [*Larix laricina* (Du Roi) K. Koch.], with an understory of herbs and a mat composed of sphagnum and sedges (*Carex* spp.). The S2 watershed was of particular interest to this study because it has a large historical database concerning soils, hydrology, and chemical cycling (Verry and Timmons, 1982; Urban et al., 1989; Grigal, 1991). Climatic and hydrologic data have been collected continuously at monitoring stations since 1961.

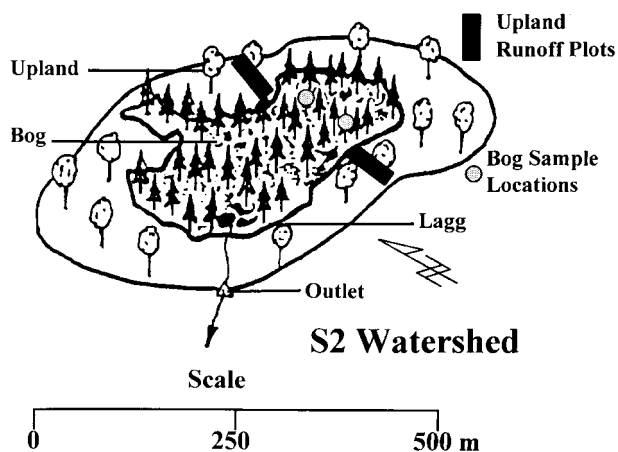


Fig. 2. Schematic of the S2 watershed at the Marcell Experimental Forest.

Climate

The climate of the Marcell Experimental Forest is sub-humid continental, with wide and rapid diurnal and seasonal temperature fluctuations. The average annual air temperature is 2°C, with extremes of -46 and 40°C. Average January and July temperatures are -14 and 19°C, respectively. Average annual precipitation at the Marcell Experimental Forest is 77.5 cm, with 75% occurring in the snow-free period (mid April to early November) (Verry et al., 1988).

Soils

Soils of the S2 watershed are formed mostly from Wisconsin glacial drift. The upper 20 to 30 cm of the upland soil material is fine sandy loam with a surface of eolian loess and a subsurface of glacial till (Warba series, fine-loamy, mixed, superactive, frigid Haplic Glossudalfs). Peatland soils are derived from organic accumulation within an ice-block depression (Loxley series, dysic frigid Typic Haplosaprists) and are from sphagnum moss and herbaceous plants over limnic materials over glacial sediments (Verry and Timmons, 1982). Peat depth ranges from 3 to 9 m through the center of the bog.

Hydrologic Data Collection

The measurement of the open precipitation, throughfall, and stemflow has been described in Kolka et al. (1999a). Briefly, cover percentages and the spatial extent of the three watershed components (upland, bog, and lagg) were used to representatively place 10 throughfall and stemflow collectors. A throughfall collector was also placed in an opening, ≈1.5 km from the S2 watershed, where the National Atmospheric Deposition Program (NADP) monitors HgT in wet deposition. Weighted means, based on the areal proportion represented by each collector, were used to estimate the deposition of HgT and OC to the upland, bog, and lagg.

A continuous recording stream gauge has monitored flow at a 120° V-notch weir at a stream just below the bog outlet since 1961 (Fig. 2). Flow tends to cease for ≈2 to 4 mo during the winter (December-March), providing a hydroperiod of ≈8 to 10 mo depending on the climate of a particular year. In the upland, pairs of surface and subsurface runoff plots were established in 1971 and have been monitored and sampled weekly and after storm events (Verry and Timmons, 1982). Upland runoff plots, 0.004 and 0.003 ha in size on slopes of 22 and 26%, are oriented based on aspect, one northerly and one southerly (Fig. 2). Plots extend from the top to the base of the slope near the peatland. A steel box below the organic O horizon, which empties to a polyvinyl chloride (PVC) pipe, collects surface runoff from the bordered plots. The PVC pipe is connected to a bucket that overflows into a polyethylene collection tank. Subsurface runoff (interflow) is collected in a 1.82-m stainless steel wellpoint placed horizontally at the top of a slowly permeable Bt horizon. The wellpoint, set in a bed of silica sand, is connected by a PVC pipe and flow is collected similarly to surface runoff. The total amount of upland runoff was estimated using a streamflow separation technique applied to the watershed stream hydrograph (Verry et al., 1988). Monthly partitioning of upland flow between surface and subsurface runoff was estimated with the Peatland Hydrologic Impact Model (PHIM), originally designed and validated for both the mineral and organic soil components in the S2 watershed (Barten, 1985; Guertin et al., 1987). Flow from the bog was the difference between that at the outlet and that predicted from the upland.

Sampling and Pretreatment Methods

Throughfall and stemflow samples were collected every 2 wk throughout the snow-free period in 1995 (19 April–14 November) except at the NADP open precipitation site where sampling was weekly. Snow samples were collected from the open, upland, and bog in 1995 and adjacent to each throughfall collector in 1996 (Kolka et al., 1999a). Stream, surface runoff, and interflow samples were collected every 2 wk during the ice-free (flow) period except during periods of high flow in the spring when collection intensity increased. Surface runoff and interflow were also sampled on an event basis. Bog samples were collected every 2 wk during the ice-free period. Runoff in the bog was sampled with a teflon ladle from holes excavated with gloved hands to ≈ 30 cm. Bog samples were collected 25 m from the lagg towards the center of the bog. Two bog water samples were collected during each sampling, one associated with each of the upland runoff collectors (Fig. 2). Samples collected for HgT analysis were collected in acid-washed 125-mL teflon bottles, acidified with 0.5 mL of high purity HCl within hours after collection, and frozen upon arrival at the laboratory. Bromine chloride was added directly to the frozen samples prior to analysis. Freezing did not affect HgT concentrations (Kolka et al., 1999b). The DOC and TOC samples were collected in acid-washed 250-mL polyethylene bottles and also frozen upon arrival to the laboratory.

Total Mercury and Organic Carbon Analysis

Rigorously tested cleaning and analytical procedures were used throughout sample handling and analysis. Samples collected for the analysis of HgT were not filtered because of potential contamination (Kolka, 1996). Total Hg was measured by double amalgamation cold vapor atomic fluorescence spectrometry in a cleanroom (Bloom and Crecelius, 1983). Reagents were routinely analyzed and cleaned of HgT, and sets of standards and blanks were analyzed several times each day. A minimum of 20% duplicates were included within each sample train. Duplicate analysis of 193 open precipitation, throughfall, and stemflow samples had a mean concentration for all samples of 37.0 ng L^{-1} , and a pooled standard error (SE) of 3.3%. Duplicate analysis of 120 stream and runoff samples averaged 12.50 ng L^{-1} (SE = 2.3%).

Samples measured for DOC were filtered through $0.7\text{-}\mu\text{m}$ glass filters and analyzed by a low temperature Dohrmann DC-80 total organic C analyzer (Dohrmann, Santa Clara, CA). Unfiltered (TOC) samples were measured using the same procedure. The mean concentration for all samples was 41.4 mg L^{-1} , with a SE of 3.27% for duplicates ($n = 58$). Particulate organic C was calculated as the difference in concentration between TOC and DOC.

Statistical Analysis

Monthly HgT and OC fluxes were calculated by multiplying mean monthly concentrations by monthly water flows (Fig. 1). The water flow volumes were from the hydrograph separation technique for bog runoff and the PHIM model for upland surface and subsurface runoff. Linear regression was used to compare HgT and OC concentrations and fluxes. We included 3 yr of streamflow, upland surface runoff, and interflow data (1993–1995) in our HgT and OC regression analysis. Open deposition, throughfall, stemflow, and bog waters were sampled only in 1995; hence, that mass balance for all components is only presented for 1995. Concentrations of HgT and OC in the bog were measured from May through October 1995. The volume-weighted mean for those months was used to estimate concentrations in March, April, November, and December. Student's *t*-tests were used to compare monthly concentrations

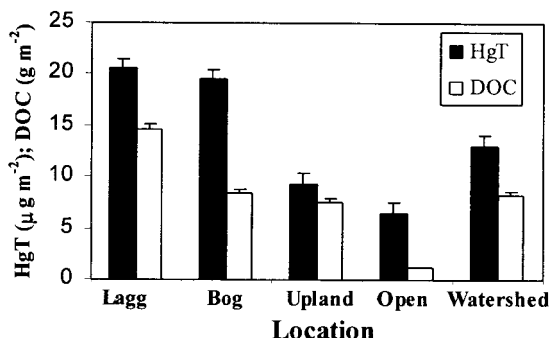


Fig. 3. Throughfall and stemflow flux of total Hg (HgT) and dissolved organic C (DOC) in the S2 watershed and precipitation in a nearby opening in 1995. Watershed is an areal weighted average. Error bars are standard errors.

and fluxes within and among hydrologic compartments. Uncertainty for depositional volume (i.e., open precipitation, throughfall, and stemflow) was considered to be the SE among the annual volumes of collectors within a cover type (Kolka et al., 1999a). Uncertainty for areal fluxes of runoff from the upland and bog were conservatively estimated at 10% as no ground truth was available to determine error. A runoff flux error of 10% is consistent with PHIM model calibrations for the S2 watershed (Guertin et al., 1987). Flux uncertainty is the result of the propagation of volume errors with laboratory uncertainty and sample concentration variability within months (Kolka, 1996).

RESULTS AND DISCUSSION

Open Precipitation, Throughfall, and Stemflow

Results of the precipitation, throughfall, and stemflow components of the HgT and OC mass balance can be found in Kolka et al. (1999a). We will briefly review those results and place those results into the context of the watershed mass balance. Total Hg concentrations in upland throughfall were ≈ 1.6 times those in the open, while those in the bog and lagg throughfall were 2.1 and 3.1 times higher, presumably because HgT-containing particulates (dry deposition) were washed from the canopy during precipitation events. Stemflow is an important source of HgT to the watershed, adding $\approx 8\%$ to that deposited in the open. Total throughfall plus stemflow deposition of HgT in the deciduous upland was 1.4 times that in the open, while throughfall plus stemflow deposition in the conifer bog and lagg were 3.0 and 3.2 times that of the deposition in the opening (Fig. 3). In 1995, twice as much HgT was deposited in the forested S2 watershed than in the open (Fig. 3).

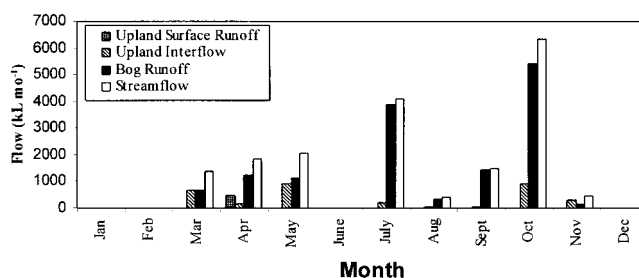


Fig. 4. Monthly flow volumes for the S2 watershed in 1995.

Total DOC throughfall plus stemflow deposition in the upland was 6.3 times that in the open, while throughfall plus stemflow deposition in the bog and lagg were 7.0 and 12 times that in the open (Fig. 3). During 1995,

6.8 times as much DOC was deposited in the S2 watershed than in the open (Fig. 3).

Dissolved organic C concentrations explained 36 to 57% of the variation in HgT concentration for open precipitation, upland throughfall, and bog throughfall ($P < 0.05$). Significant positive relationships also existed between HgT and DOC concentrations in stemflow, with 83% of the variability in HgT concentration explained by DOC concentration when all species were grouped (Kolka et al., 1999a). The extent of HgT complexation with OC appears to be related to the residence time waters are in contact with vegetation, with relationships becoming stronger in stemflow where contact time was longer than throughfall. Because of low and undetectable POC concentrations, we found weak relationships with HgT.

Terrestrial Inputs to the Lagg

In 1995 flow varied seasonally, with peaks in upland runoff occurring during spring and fall (Fig. 4). Upland surface runoff was only important during snowmelt in the spring. For most of the year, bog runoff is the dominant source of flow to the lagg. The annual contributions

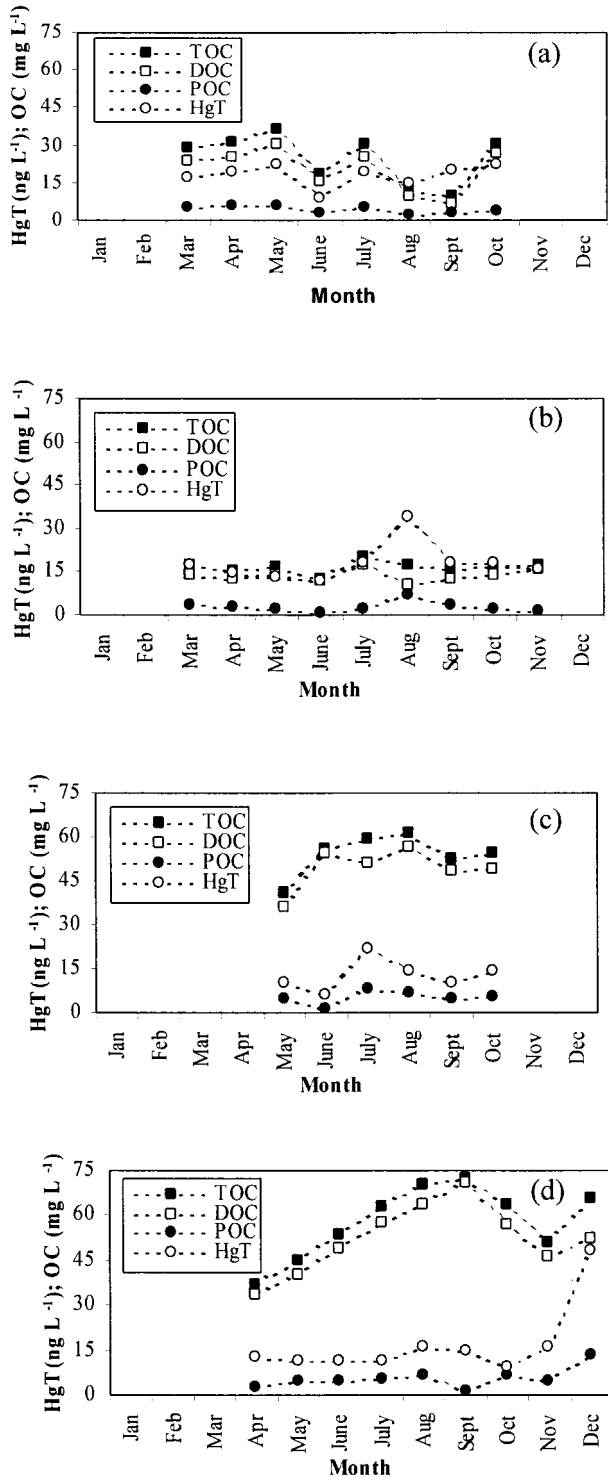


Fig. 5. Mean monthly concentrations of total Hg (HgT) and organic C (OC) in (a) upland surface runoff, (b) interflow, (c) bog runoff, and (d) streamflow for the S2 watershed in 1995. TOC, total organic C; DOC, dissolved organic C; POC, particulate organic C; HgT, total Hg.

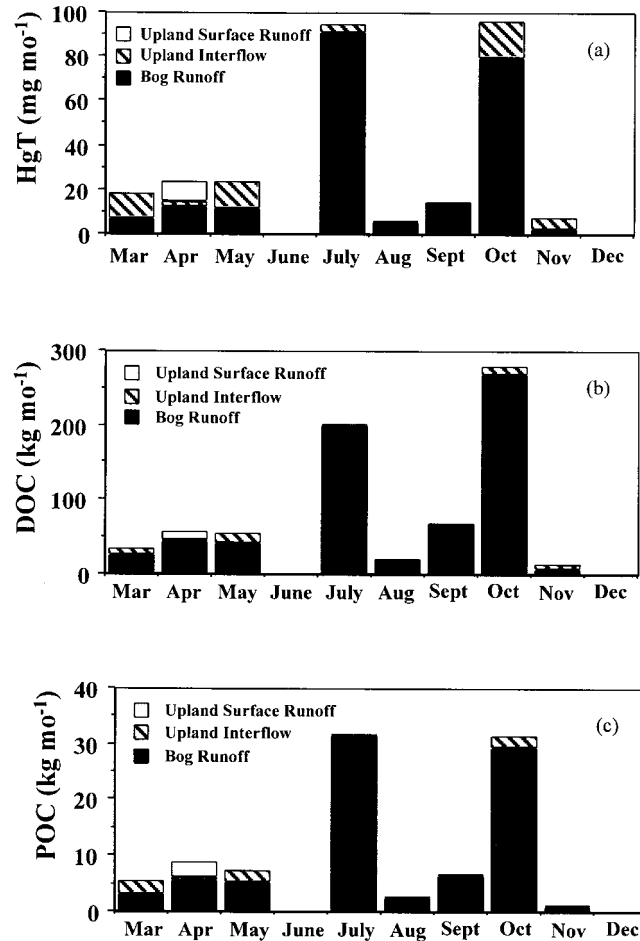


Fig. 6. Monthly fluxes of total Hg (HgT) and organic C (OC) in (a) upland surface runoff, (b) upland interflow, and (c) bog runoff for the S2 watershed in 1995. Mean annual concentrations of HgT and OC were applied to bog flows in March, April, November, and December to estimate fluxes for those months.

to the total watershed water yield are 500, 3250, and 14 300 kL for upland surface runoff, upland interflow, and bog runoff, respectively. Poor relationships existed between terrestrial flows and HgT and OC concentrations; none explained >50% of the variation.

Distinct seasonal trends were not apparent for HgT and OC concentrations in upland surface runoff or interflow (Fig. 5). Concentrations of both HgT and OC in surface runoff were more variable than those in interflow. Concentrations of HgT and POC in bog runoff peaked in July, the summer month when flow was greatest (Fig. 5). High flow may have mobilized more particulates, leading to higher HgT concentrations.

Because they are driven by flow, monthly fluxes of HgT and OC in upland runoff peaked in spring and fall (Fig. 6). Upland surface runoff flux of HgT and OC was only important in April, when the bulk of snowmelt occurred. Upland surface runoff accounts for only 13% of the total upland flow, but for 15% of the HgT, 22% of the DOC, and 26% of the POC fluxes. Total upland fluxes account for 21% of the total flow to the lagg, but only for 16% of the HgT, 7% of the DOC, and 11% of the POC fluxes. Upland runoff accounts for a greater proportion of HgT than OC, indicating that complexes of OC are relatively rich in HgT. Bog runoff dominates both HgT and OC transport (Fig. 6), accounting for 63% of the flow to the lagg, 57% of the HgT, 84% of the DOC, and 83% of the POC. The remainder of the inputs to the lagg are contributed from throughfall and stemflow in the lagg itself. Bog runoff to the lagg accounts for a greater proportion of OC than HgT, indicating that complexes of OC are relatively low in HgT. Total Hg and OC fluxes were divided by the area of the bog and upland to calculate annual areal fluxes in each landscape type (Table 1). For 1995, bog runoff was the main vector by which HgT and OC were transported to the stream.

Annual areal fluxes of HgT in upland runoff for 1995 (Table 1) are somewhat lower than those reported in two Swedish studies (1.4 and $3.4 \mu\text{g m}^{-2} \text{yr}^{-1}$) (Aastrup et al., 1991; Lee et al., 1994). Upland HgT fluxes for S2 in 1993 ($1.74 \mu\text{g m}^{-2} \text{yr}^{-1}$) and 1994 ($3.91 \mu\text{g m}^{-2} \text{yr}^{-1}$) were similar to those in Sweden. Bog runoff had much higher areal fluxes of HgT and OC than upland runoff because of higher flow (Table 1). The total runoff of HgT from the watershed falls within the range of literature values for watershed loading of HgT to streams (0.2 – $4.4 \mu\text{g m}^{-2} \text{yr}^{-1}$; Mierle, 1990; St. Louis et al., 1994; Lee et al., 1995).

Total mercury concentration was poorly correlated

($r^2 < 0.25$) with TOC and DOC concentration in terrestrial waters, but was significantly correlated with POC concentration. Total Hg and POC concentrations in upland surface runoff and interflow are significantly related (Fig. 7). In our unfiltered samples, if we assume that all HgT is complexed with OC, the slope represents the nanograms of HgT associated with each milligram of POC and the y -intercept can be interpreted as the concentration of HgT in solution that is associated with DOC (Kolka et al., 1999b). This is a fair assumption considering the majority of HgT present in the terrestrial system occurs as Hg^{2+} and because of the high affinity of Hg^{2+} for organic matter (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. Because there is little covariance between POC and DOC ($r^2 = 0.06$ for upland surface runoff and $r^2 = 0.00$ for interflow), an estimate of the fractions of HgT associated with each organic fraction can be made for S2. In upland surface runoff, $\approx 54\%$ of HgT transported was associated with POC (46% with DOC), while in interflow $\approx 46\%$ was associated with POC (54% with DOC). In the upland, both DOC and POC have nearly equal influence on the transport of HgT.

Little covariance also existed between POC and DOC in runoff from the bog dome ($r^2 = 0.01$). Although we only have observations for 6 mo, the data indicate that >90% of the HgT transported in bog runoff is associated with POC (Fig. 7). Although the absolute value is uncertain, it is clear that the particulate organic fraction is very important in HgT transport from the bog.

Streamflow

Total organic C and DOC concentrations showed strong seasonal trends in stream water with peak concentrations during the summer, while HgT and POC concentrations were more variable with peak concentrations in December (Fig. 5). The peaks in TOC and DOC concentrations in summer are related to the period of maximum decomposition. Concentrations of Hg and POC are relatively stable except in December. We suspect the December rise in Hg and OC is the result of water flowing from beneath the soil frost layer. At the onset of peatland freezing, clear water ice forms first, with colloid-rich water freezing later. Prior to the colloid-rich water freezing, it is concentrated in Hg and OC and flows beneath the clear ice to the stream. Streamflow concentrations of HgT in S2 (mean annual

Table 1. Area weighted annual fluxes of total Hg (HgT) and organic C in upland surface runoff, interflow, and bog runoff for the S2 watershed in 1995.

	Flow	HgT	TOC [†]	DOC [†]	POC [†]
	L m^{-2}	$\mu\text{g m}^{-2}$	g m^{-2}		
Upland surface runoff	7.8 (0.8) [‡]	0.15 (0.02)	0.24 (0.03)	0.20 (0.02)	0.04 (0.00)
Upland interflow	51 (5.1)	0.83 (0.08)	0.86 (0.09)	0.73 (0.07)	0.13 (0.01)
Upland total	59 (5.2)	0.98 (0.08)	1.10 (0.09)	0.93 (0.07)	0.17 (0.01)
Bog	490 (50)	4.78 (0.48)	31.13 (3.11)	28.43 (2.84)	2.69 (0.27)
Upland + Bog	200 (30)	2.24 (0.40)	11.11 (1.96)	10.09 (1.78)	1.01 (0.18)

[†] TOC, total organic C; DOC, dissolved organic C; POC, particulate organic C.

[‡] Standard error in parentheses.

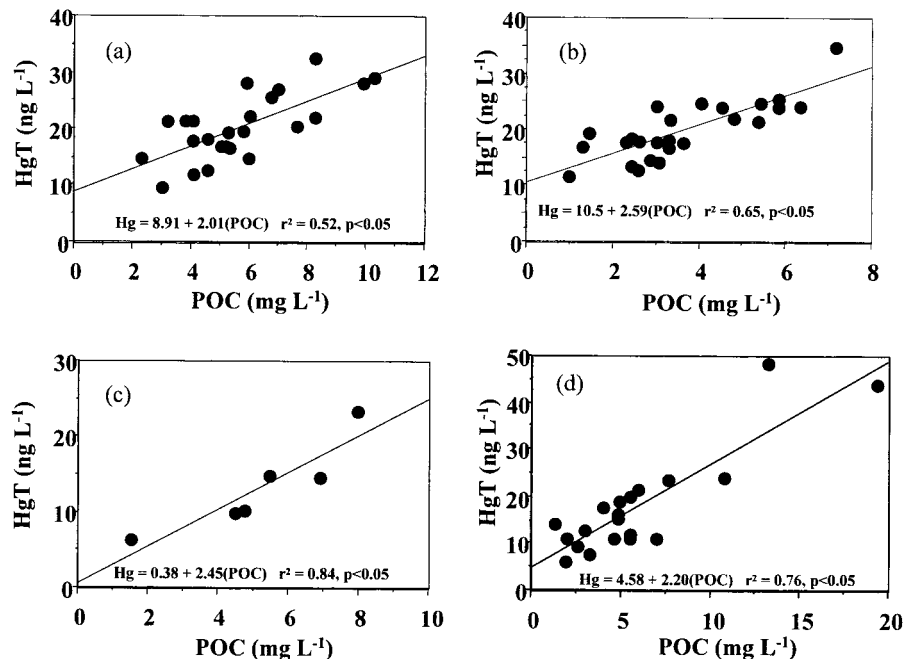


Fig. 7. Relationships between mean monthly total Hg (HgT) and particulate organic C (POC) concentration in (a) upland surface runoff, (b) upland interflow, (c) bog flow, and (d) streamflow for the S2 watershed.

volume weighted concentration = 15.1 ng L^{-1}) were somewhat higher than those reported in the literature ($1.3\text{--}13.1 \text{ ng L}^{-1}$; Mierle, 1990; Lee and Iverfeldt, 1991; St. Louis et al., 1994; Krabbenhoft et al., 1995; Lee et al., 1995).

Fluxes of HgT and OC in the stream should mirror the inputs to the lagg because the lagg is the proximate source of flow for the stream. For POC this is the case; inputs to the lagg annually account for 106% of POC found in the stream (Fig. 8; Table 2). For DOC, the lagg annually accounts for 85% of that in the stream (Fig. 8; Table 2). When compared with the sum of inputs, it appears the lagg is a source of DOC. For HgT, the lagg accounts for 184% of the HgT measured in the stream (Fig. 8; Table 2). Either soil accumulation or volatilization losses probably account for this difference (see discussion below).

Although mean monthly HgT and DOC ($r^2 = 0.00$) or TOC ($r^2 = 0.05$) concentration were poorly correlated in stream water, significant relationships occurred between POC and HgT (Fig. 7) with little covariance between POC and DOC in stream waters ($r^2 = 0.02$). The relationship estimates that 30% of the HgT in the stream is associated with DOC and 70% is associated with POC. It is clear that OC, both particulate and dissolved, has a significant influence on the hydrologic transport of HgT through forested watersheds.

The Hydrologic Mass Balance

The forest canopy is a significant source of HgT, but the bulk of HgT deposition is not transported from the upland or bog; hence, the upland and bog soils are sinks for HgT (Table 2). Although the bog is approximately one-half the size of the upland, it contributes more than three times more HgT to the lagg. Total Hg deposited in

the upland or bog is volatilized back to the atmosphere, transported via runoff, or stored in the soil. If the difference between canopy inputs and runoff is considered to only add to soil storage, the rates of Hg accumulation are 8 and $12 \mu\text{g m}^{-2} \text{ yr}^{-1}$ for the upland and bog, respectively. Upland soils in this region have accumulated 1 to $17 \mu\text{g HgT m}^{-2} \text{ yr}^{-1}$ in the past 35 to 165 yr (Nater and Grigal, 1992). Bog soils in the area have accumulated 29 to $71 \mu\text{g HgT m}^{-2} \text{ yr}^{-1}$ in the past 90 yr (Benoit et al., 1994). Although some HgT volatilization is probably occurring, net accretion in soil could explain the entire difference. Alternatively, if the soil is considered to be in a steady state with no net accretion, the excess HgT in the system would define the maximum potential volatilization rates. Rates would range from $-0.1 \text{ ng m}^{-2} \text{ h}^{-1}$ in April to $3.9 \text{ ng m}^{-2} \text{ h}^{-1}$ in July for the upland and $-2.1 \text{ ng m}^{-2} \text{ h}^{-1}$ in October to $4.9 \text{ ng m}^{-2} \text{ h}^{-1}$ in August for the bog. These rates fall within the range reported in the literature for uncontaminated soils ($-9\text{--}29 \text{ ng m}^{-2} \text{ h}^{-1}$; Kim et al., 1995). The fate of HgT in the S2 watershed soils is probably a combination of the two processes of storage and volatilization. Because of differences in amount of C and the microbial conditions between upland and peatland soils, we suspect the bulk of HgT added to the upland is volatilized, while the bulk of HgT deposited in the bog is probably added to soil storage.

Annually, the sum of terrestrial and atmospheric influxes into the lagg accounts for 184% of the HgT fluxes at the stream outlet, even though the lagg is the source of flow for the stream (Table 2). We believe the bulk of these losses of HgT from the lagg can be attributed to the occurrence of either soil accumulation or volatilization between our sampling points higher up in the watershed and the outlet. The soils in the lagg are or-

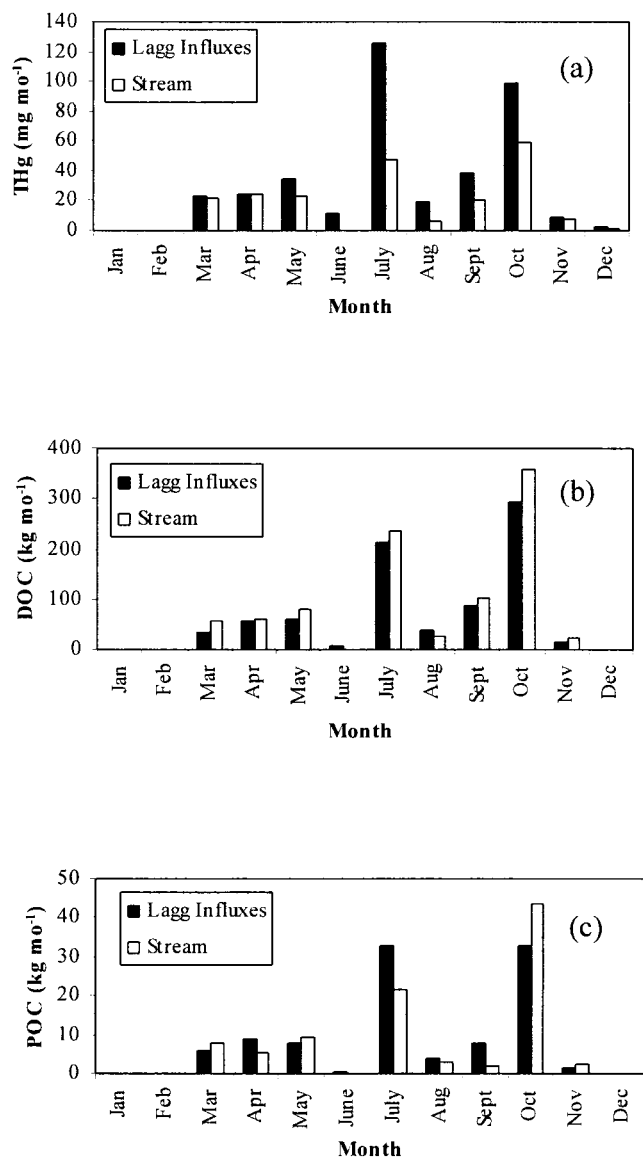


Fig. 8. Monthly comparison of total Hg (HgT), dissolved organic C (DOC), and particulate organic C (POC) influxes to the (a) lag and those fluxes in (b) streamflow.

ganic and probably have a high ability to complex HgT. If we assume soil accumulation was the only loss of Hg, the lag soil would accumulate $\approx 35 \mu\text{g HgT m}^{-2} \text{ yr}^{-1}$, within the range of that reported earlier for bog soils (Benoit et al., 1994). If volatilization is considered to be the only Hg loss, the mean rate from the lag is $6.8 \text{ ng m}^{-2} \text{ h}^{-1}$, somewhat greater than that estimated earlier for upland and bog soils in S2 but still within the range reported by Kim et al. (1995). Both processes, soil accumulation and volatilization, are probably contributing to losses in the lag.

The forest canopy is also an important source of DOC and POC (Table 2). The upland soil is the only sink for DOC and POC in the watershed. The bulk of OC deposited in the upland is probably mineralized by microbial respiration instead of being added to the soil pool. Bog runoff to the lag and ultimately to the stream is the most important transport mechanism for OC in

Table 2. Annual hydrologic fluxes of total Hg (HgT), dissolved organic C (DOC), and particulate organic C (POC) in the S2 watershed for 1995.

	HgT	DOC	POC
	mg	kg	
Upland Fluxes (6.2 ha)			
Open deposition	403.0 (13.0) [†]	75.0 (13.7)	4.9 (1.1)
Throughfall + stemflow	577.8 (19.1)	525.1 (16.5)	31.8 (1.0)
Surface runoff	9.6 (1.2)	13.0 (1.3)	2.9 (0.2)
Interflow	53.8 (5.0)	47.0 (4.3)	8.4 (0.6)
Bog Fluxes (3.0 ha)			
Open deposition	195.0 (6.4)	36.3 (6.3)	2.2 (0.6)
Throughfall + stemflow	585.3 (27.6)	246.0 (11.7)	15.8 (0.8)
Bog runoff	221.6 (14.4)	671.5 (85.2)	84.2 (8.1)
Lagg Fluxes (0.5 ha)			
Open deposition	32.5 (1.1)	6.1 (1.1)	0.6 (0.2)
Throughfall + stemflow	102.8 (3.7)	72.7 (2.3)	5.8 (0.2)
Sum of Inputs to the Lagg and Stream Fluxes			
Lagg (Sum)	387.8 (23.8)	804.2 (91.2)	101.3 (9.2)
Stream fluxes	210.7 (34.9)	947.6 (35.8)	95.4 (6.8)
Sources[‡]			
Upland canopy	174.8	450.1	26.9
Bog canopy	390.3	209.7	13.6
Lagg canopy	70.3	66.6	5.2
Bog soil		425.5	68.4
Lagg soil		143.4	
Sinks[§]			
Upland soil	514.4	465.1	20.5
Bog soil	363.7		
Lag soil	177.1		5.9
Sources—sinks	-419.8	830.2	87.7

[†] Standard error in parentheses.

[‡] Sources = (throughfall + stemflow) - open deposition, runoff - (throughfall + stemflow), stream - lagg.

[§] Sinks = (throughfall + stemflow) - runoff, lagg - stream.

the S2 watershed. The sum of fluxes from the upland, bog, and deposition to the lag, agrees well with that measured in the stream (DOC = 85% of stream, POC sum = 106% of stream). Although the SEs overlap for POC, it does appear that DOC is produced between the point where we measured the inputs to the lag in the upper part of the watershed and the outlet (Fig. 2).

CONCLUSIONS

In this study we have identified the major hydrologic fluxes responsible for the transport of HgT to surface waters in a typical headwater catchment in the western Great Lakes region, an area well known for fish consumption advisories because of high Hg levels. In addition, we have developed a mass balance of HgT and OC and identified sinks and sources in the watershed and speculated on the fate of unaccounted fluxes. It is clear that OC, both particulate and dissolved, and hydrology have a significant influence on the transport of HgT through forested watersheds. The results of this study indicate that POC is not only an important vector of HgT transport in streams, but POC also plays an important role in terrestrial transport. Watershed disturbances that stimulate the transport of particulates and/or lead to higher water yields (e.g., construction, conversion from forest to agriculture, or forest harvesting) will probably lead to greater HgT in runoff and subsequently in surface waters. Strategies that control or lessen partic-

ulate transport to surface waters and wetlands, such as the use of buffer strips or erosion control devices, should be considered to minimize HgT transport.

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REFERENCES

- Aastrup, M., J. Johnson, E. Bringmark, I. Bringmark, and A. Iverfeldt. 1991. Occurrence and transport of mercury within a small catchment area. *Water Air Soil Pollut.* 56:155-167.
- Barten, P.K. 1985. Testing and refinement of the Peatland Hydrologic Impact Model. M.S. thesis. Univ. of Minnesota, St. Paul.
- Benoit, J.M., W.F. Fitzgerald, and A.W.H. Damman. 1994. Historical atmospheric mercury deposition in the mid-continental U.S. as recorded in an ombrotrophic peat bog. p. 187-202. *In* C.J. Watras and J.W. Huckabee (ed.) *Mercury pollution: Integration and synthesis*. Lewis Publ., Chelsea, MI.
- Bloom, N.S., and E.A. Creelius. 1983. Determination of mercury in seawater at subnanogram per litre levels. *Mar. Chem.* 14:49-59.
- Branfireun, B.A., A. Heyes, and N.T. Roulet. 1996. The hydrology and methylmercury dynamics of a Precambrian shield headwater peatland. *Water Resour. Res.* 32:1785-1794.
- Driscoll, C.T., V. Blette, C. Yan, C.L. Schofield, R. Munson, and J. Holsapple. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. *Water Air Soil Pollut.* 80:499-508.
- Driscoll, C.T., C. Yan, C.L. Schofield, R. Munson, and J. Holsapple. 1994. The chemistry and bioavailability of mercury in remote Adirondack lakes. *Environ. Sci. Technol.* 28:136-143.
- Fitzgerald, W.F. 1986. Cycling of mercury between the atmosphere and oceans. p. 363-408. *In* P. Buat-Ménard (ed.) *The role of air-sea exchange in geochemical cycling*. D. Reidel, Boston.
- Grigal, D.F. 1991. Elemental dynamics in forested bogs in northern Minnesota. *Can. J. Bot.* 69:539-546.
- Grigal, D.F., E.A. Nater, and P.S. Homann. 1994. Spatial distribution patterns of mercury in an east-central Minnesota landscape. p. 305-312. *In* C.J. Watras and J.W. Huckabee (ed.) *Proceedings on international conference on mercury as a global pollutant*. Monterey, CA. 31 May-4 June 1992. Electric Power Research Inst., Palo Alto, CA.
- Guertin, D.P., P.K. Barten, and K.N. Brooks. 1987. The peatland hydrologic impact model: Development and testing. *Nordic Hydrol.* 18:79-100.
- Hanson, P.J., S.E. Lindberg, T.A. Tabberer, J.G. Owens, and K.-H. Kim. 1995. Foliar exchange of mercury vapor: Evidence for a compensation point. *Water Air Soil Pollut.* 80:373-382.
- Hudson, R.J.M., S.A. Gherini, W.F. Fitzgerald, and D.B. Porcella. 1995. Anthropogenic influences on the global mercury cycle: A model-based analysis. *Water Air Soil Pollut.* 80:265-272.
- Hultberg, H., A. Iverfeldt, and Y.H. Lee. 1994. Methylmercury input/output and accumulation in forested catchments and critical loads for lakes in Southwestern Sweden. p. 313-322. *In* C.J. Watras and J.W. Huckabee (ed.) *Proceedings on international conference on mercury as a global pollutant*. Monterey, CA. 31 May-4 June 1992. Electric Power Research Inst., Palo Alto, CA.
- Hurley, J.P., J.M. Benoit, C.L. Babiarz, M.M. Shafer, A.W. Andren, J.R. Sullivan, R. Hammond, and D.A. Webb. 1995. Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environ. Sci. Technol.* 29:1867-1875.
- Iverfeldt, A. 1991. Mercury in forest canopy throughfall water and its relation to atmospheric deposition. *Water Air Soil Pollut.* 56:553-564.
- Johansson, K., M. Aastrup, A. Andersson, L. Bringmark, and A. Iverfeldt. 1991. Mercury in Swedish forest soils and waters—Assessment of critical load. *Water Air Soil Pollut.* 56:267-281.
- Johansson, K., and A. Iverfeldt. 1994. The relationship between mercury content in soil and the transport of mercury from small catchments in Sweden. p. 323-328. *In* C.J. Watras and J.W. Huckabee (ed.) *Proceedings on international conference on mercury as a global pollutant*. Monterey, CA. 31 May-4 June 1992. Electric Power Research Inst., Palo Alto, CA.
- Kabata-Pendias, A., and H. Pendias. 1992. *Trace elements in soils and plants*. CRC Press, Boca Raton, FL.
- Kim, K.-H., S.E. Lindberg, and T.P. Meyers. 1995. Micrometeorological measurements of mercury vapor fluxes over background forest soils in eastern Tennessee. *Atmos. Environ.* 29:267-282.
- Kolka, R.K. 1996. Hydrologic transport of mercury through forested watersheds. Ph.D. thesis. Univ. of Minnesota, St. Paul.
- Kolka, R.K., E.A. Nater, D.F. Grigal, and E.S. Verry. 1999a. Atmospheric input of mercury and organic carbon into a forested upland/bog watershed. *Water Air Soil Pollut.* 113:273-294.
- Kolka, R.K., E.S. Verry, D.F. Grigal, and E.A. Nater. 1999b. Mercury and organic carbon relationships in streams draining forested upland/peatland watersheds. *J. Environ. Qual.* 28:766-775.
- Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley, and A.W. Andren. 1995. Mercury cycling in the Allequash Creek watershed, Northern Wisconsin. *Water Air Soil Pollut.* 80:425-433.
- Lamborg, C.H., M.E. Hoyer, G.J. Keeler, I. Olmez, and X. Huang. 1994. Particulate-phase mercury in the atmosphere: Collection/analysis method development and applications. p. 251-260. *In* C.J. Watras and J.W. Huckabee (ed.) *Proceedings on international conference on mercury as a global pollutant*. Monterey, CA. 31 May-4 June 1992. Electric Power Research Inst., Palo Alto, CA.
- Lee, Y.-H., K. Bishop, C. Pettersson, A. Iverfeldt, and B. Allard. 1995. Subcatchment output of mercury and methylmercury at Svartberget in Northern Sweden. *Water Air Soil Pollut.* 80:189-198.
- Lee, Y.-H., G.C. Borg, A. Iverfeldt, and H. Hultberg. 1994. Fluxes and turnover of methylmercury: mercury pools in forest soils. p. 329-342. *In* C.J. Watras and J.W. Huckabee (ed.) *Proceedings on international conference on mercury as a global pollutant*. Monterey, CA. 31 May-4 June 1992. Electric Power Research Inst., Palo Alto, CA.
- Lee, Y.-H., and A. Iverfeldt. 1991. Measurement of methylmercury and mercury in runoff, lake and rain waters. *Water Air Soil Pollut.* 56:309-321.
- Lindberg, S.E., J.G. Owens, and W.J. Stratton. 1994. Application of throughfall methods to estimate dry deposition of mercury. p. 261-272. *In* C.J. Watras and J.W. Huckabee (ed.) *Proceedings on international conference on mercury as a global pollutant*. Monterey, CA. 31 May-4 June 1992. Electric Power Research Inst., Palo Alto, CA.
- Lindberg, S.E., R.R. Turner, T.P. Meyers, G.E. Taylor, Jr., and W.H. Schroeder. 1991. Atmospheric concentrations and deposition of HgT to a deciduous forest at Walker Branch Watershed, Tennessee, USA. *Water Air Soil Pollut.* 56:577-594.
- Lindqvist, O. 1991. Mercury in the Swedish environment. *Water Air Soil Pollut.* 55:23-32.
- Meili, M., A. Iverfeldt, and L. Hakanson. 1991. Mercury in the surface water of Swedish forest lakes—Concentrations, speciation and controlling factors. *Water Air Soil Pollut.* 56:439-453.
- Mierle, G. 1990. Aqueous inputs of mercury to precambrian shield lakes in Ontario. *Environ. Toxicol. Chem.* 9:843-851.
- Munthe, J., H. Hultberg, and A. Iverfeldt. 1995. Mechanisms of deposition of methylmercury and mercury to coniferous forests. *Water Air Soil Pollut.* 80:363-371.
- Nater, E.A., and D.F. Grigal. 1992. Regional trends in mercury distribution across the Great Lakes states, north central USA. *Nature* 358:139-141.
- St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom, and R.J. Flett. 1994. Importance of wetlands as sources of methylmercury to boreal forest ecosystems. *Can. J. Fish Aquat. Sci.* 51:1065-1076.
- St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, R.J. Flett, and N.T. Roulet. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ. Sci. Technol.* 30:2719-2729.
- Schuster, E. 1991. The behavior of mercury in the soil with special

emphasis on complexation and adsorption processes—A review of literature. *Water Air Soil Pollut.* 56:667–680.

Sorensen, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber, and G.R. Rapp, Jr. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environ. Sci. Technol.* 24:1716–1727.

Steinnes, E., and E.M. Andersson. 1991. Atmospheric deposition of mercury in Norway: Temporal and spatial trends. *Water Air Soil Pollut.* 56:391–404.

Swain, E.B., D.R. Engstrom, M.E. Brigham, T.A. Henning, and P.L. Brezonik. 1992. Increasing rates of atmospheric mercury deposition

in midcontinental North America. *Science* (Washington, DC) 257:784–787.

Urban, N.R., S.E. Bayley, and S.J. Eisenreich. 1989. Export of dissolved organic carbon and acidity from peatlands. *Water Resour. Res.* 25:1619–1628.

Verry, E.S., K.N. Brooks, and P.K. Barten. 1988. Streamflow response from an ombrotrophic mire. p. 25–29. *In Proc. Sym. Hydrology of Wetlands in Temperate and Cold Climates*. Vol. 1. Joensuu, Finland. 8 June 1988. Academy of Finland, Helsinki, Finland.

Verry, E.S., and D.R. Timmons. 1982. Waterborne nutrient flow through an upland-peatland watershed in Minnesota. *Ecology* 63:1456–1467.

Nutrient Retranslocation Response of *Picea mariana* Seedlings to Nitrogen Supply

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ABSTRACT

The hypotheses that retranslocation is controlled by soil nutrient availability or plant nutrient reserves were tested under field conditions for one growing season using nutrient-loaded and non-loaded (conventional) black spruce [*Picea mariana* (Mill.) BSP] seedlings planted on a poor, medium, and rich fertility soil created by equivalent applications of 0, 200, and 400 kg N ha⁻¹, respectively. Growth and nutrient uptake increased with N supply, and was consistently higher in loaded than conventional seedlings, demonstrating the advantage of nutrient loading practices to accelerate seedling growth across the range of soil N tested. Compared to the poor soil, new shoot biomass of loaded seedlings increased by 34 and 134% on the medium and rich soils, suggesting loaded seedlings may be more efficiently transplanted on more fertile sites. Net retranslocation of N, P, and K increased by 569, 185, and 102% by nutrient loading in the nursery, supporting the hypothesis of translocation driven by the magnitude of plant nutrient reserves. However, net N retranslocation diminished with time due to root system expansion that promoted uptake and reduced the need for N redistribution. Net retranslocation of N (the most limiting nutrient) declined with soil N supply, but that of P and K were relatively independent of soil fertility. Increased N availability in the soil enhanced N accumulation in the plants but lowered N retranslocation. We conclude that higher net retranslocation of N on poor soils is a phenotypic adjustment by *P. mariana* seedlings to maximize N use at low availability.

NEWLY PLANTED SEEDLINGS depend highly on retranslocation of internal nutrient reserves to sinks of new growth soon after transplanting because initial slow root development limits uptake from the soil (Burdett et al., 1984; van den Driessche, 1985; Burdett, 1990). Retranslocation can be defined as the amount of an element depleted from older plant components and made available for new growth (Lim and Cousens, 1986), and has demonstrated prime significance in the nutrient economy of plants (Kim et al., 1987).

New cultural techniques, such as nutrient loading, have been designed specifically to build higher plant nutrient reserves in seedlings during nursery culture (Timmer and Aidelbaum, 1996). These reserves are de-

pleted later to support current growth in newly transplanted seedlings. For example, nutrient-loaded seedlings depleted 67% N from old shoots to support new growth in black spruce (Malik and Timmer, 1998), and 51 to 60% in Chinese fir [*Cunninghamia lanceolata* (Lamb) Hook] (Xu and Timmer, 1999). Nutrient-loaded seedlings also grew faster, took up more nutrients, and suppressed weeds more effectively in the field (Malik and Timmer, 1998). Since nutrients often limit growth of seedlings in boreal forests under interspecific competition (Nilsson et al., 1986; Orlander et al., 1986), the higher internal reserves acquired by nutrient-loaded trees may ameliorate nutrient shortages when transplanted on such sites (Timmer, 1997; Timmer and Aidelbaum, 1996).

Malik and Timmer (1998) contend that net retranslocation is a key mechanism driving the improved transplanting growth response and competitiveness of nutrient-loaded seedlings on weed prone sites. However, the retranslocation response seems to decline with soil N availability (Timmer and Munson, 1991; Xu and Timmer, 1999), raising the question whether nutrient-loaded seedlings should be more efficiently transplanted on poor rather than rich soils? Furthermore, variability of retranslocation with soil nutrient availability is still controversial (Hawkins et al., 1999). Current work suggests that retranslocation may be regulated by soil nutrient supply, nutrient uptake rates, the size of plant nutrient reserves, and age of trees (Munson et al., 1995; Hawkins et al., 1998, 1999; Malik and Timmer, 1998), although the mechanisms involved are not well understood (Hawkins et al., 1999). Furthermore, the relative contributions of nutrients from retranslocation and from external uptake to sinks of new growth are unknown.

In this study, we used a conceptual model (Lim and Cousens, 1986) to quantify relative contributions of nutrients from net retranslocation and external uptake to new growth under field conditions and to explain the mechanisms driving retranslocation on a N supply gradient. In addition, we examined site specific planting for loaded trees and determined whether net retranslocation is controlled by plant nutrient reserves. We focused mainly on N, because this element is usually most limiting for growth of black spruce seedlings on Boreal

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