Mercury budget of an upland-peatland watershed

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Abstract. Inputs, outputs, and pool sizes of total mercury (Hg) were measured in a forested 10 ha watershed consisting of a 7 ha hardwood-dominated upland surrounding a 3 ha conifer-dominated peatland. Hydrologic inputs via throughfall and stemflow, 13 ± 0.4 μg m^{-2} yr^{-1} over the entire watershed, were about double precipitation inputs in the open and were significantly higher in the peatland than in the upland (19.6 vs. 9.8 μg m^{-2} yr^{-1}). Inputs of Hg via litterfall were 12.3 ± 0.7 μg m^{-2} yr^{-1}, not different in the peatland and upland (11.7 vs. 12.5 μg m^{-2} yr^{-1}). Hydrologic outputs via streamflow were 2.8 ± 0.3 μg m^{-2} yr^{-1} and the contribution from the peatland was higher despite its smaller area. The sum of Hg inputs were less than that in the overstory trees, 33 ± 3 μg m^{-2} above-ground, and much less than either that in the upland soil, 5250 ± 520 μg m^{-2}, or in the peat, 3900 ± 100 μg m^{-2} in the upper 50 cm. The annual flux of Hg measured in streamflow and the calculated annual accumulation in the peatland are consistent with values reported by others. A sink for Hg of about 20 μg m^{-2} yr^{-1} apparently exists in the upland, and could be due to either or both storage in the soil or volatilization.

Introduction

Most studies of mercury (Hg) in the environment have focused on the aquatic system because of the health-related aspects of methyl-Hg accumulation in fish (Fitzgerald et al. 1998; Fleming et al. 1995). Although one source of Hg to aquatic systems is direct deposition from the atmosphere, terrestrial systems are the proximate source of much of the atmospherically-deposited Hg that reaches aquatic systems (Henning et al. 1989; Lindqvist 1991). Studies in Minnesota, U.S.A., and similar areas indicate that about 25% of atmospheric Hg deposited on terrestrial basins reaches associated lakes (Mierle & Ingram 1991; Swain et al. 1992), and contributes between 25 and 60% of the total Hg loading of these lakes. In most watersheds in northern latitudes, peatlands are an important terrestrial landscape component and play an important role in cycling of Hg (St. Louis et al. 1994; Driscoll et al. 1995;

Kolka et al. 1999a). In spite of the importance of terrestrial systems to the Hg cycle, there are few studies that have comprehensively examined a single system. We have been studying Hg fluxes in a small forested upland/peatland watershed in northern Minnesota, and the data provide an overview of Hg cycling in such a system.

Methods

Site

The S2 watershed (9.7 ha) is located on the USDA Forest Service Marcell Experimental Forest (MEF), 40 km north of Grand Rapids, Minnesota (47°32′ N, 93°28′ W). The watershed contains a 3.2 ha black spruce (*Picea mariana* Mill. B.S.P.) – *Sphagnum* peatland, a bog with an outlet pH of 3.9±0.2, and a 6.5 ha upland dominated by mature trembling aspen (*Populus tremuloides* Michx.). Upland soils are Warba sandy loams (Glossic Eutrobor-alfs) with about 35% silt plus clay in the surface (Nyberg 1987). The watershed has been instrumented and studied in detail, including hydrol-ogy (Boelter & Verry 1977) and elemental cycling (Grigal 1991; Verry & Timmons 1982), including cycling of lead, an atmospherically-derived heavy metal (Urban et al. 1990). The climate of the MEF is subhumid contin-ental, with wide and rapid diurnal and seasonal temperature fluctuations. The mean 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). Mean annual precipitation is 78 cm with 75% occurring in the snow-free period (mid-April to early November).

Because the upland and the bog are floristically, topographically, and pedologically different, these two landscape components were sampled as subunits and the resulting data were weighted by area for the entire watershed. In some cases, the lagg, a narrow transition zone that separates upland from bog, was separately sampled. It is only about 5% of the area of the catchment, and data from it have been proportionally allocated to the upland and bog. Methods have been reported in detail elsewhere (Fleck 1999; Kolka 1996; Kolka et al. 1999a; Kolka et al. 1999b) and they will only briefly be outlined.

Field sampling

Atmospheric inputs
Atmospheric inputs of Hg in the open and under the forest canopy were measured by collectors similar to Swedish IVL bulk collectors (Iverfeldt 1991). Throughfall collectors were representatively placed based on a survey

of canopy and understory cover from multiple transects (66 points; Kolka et al. 1999b); five collectors in the upland, five in the bog; and an eleventh collector was rotated as a duplicate. A twelfth collector was placed in an opening approximately 1.5 km from the S2 watershed where the National Atmospheric Deposition Program (NADP) monitors wet deposition of Hg. Fourteen stemflow collectors were also installed in S2, based on a survey of canopy species and diameter distributions (Kolka et al. 1999b).

Throughfall and stemflow samples were collected biweekly throughout the snow-free period in 1995 (19 April–14 November) except at the NADP site where sampling was weekly. Snow samples were collected from the open, upland, and bog in both 1995 and 1996 when snow was at or near its maximum seasonal water content. The deposition of Hg in throughfall was calculated as a weighted mean, based on the areal proportion of cover types represented by each collector. The areal deposition of Hg in stemflow was based on the tree distributions. Total deposition to the watershed was based on the areal proportions of each landscape component, and spanned over one hydrologic year.

Litterfall

Litterfall was sampled in autumn, 1995 (8 August to 15 November). Sixty circular plastic collectors (diameter = 28.5 cm) were located at random spacings along transects across the watershed. One-third of the collectors, randomly interspersed, were designated as Hg samplers and the remainder were only used to assess litterfall mass. Collectors for Hg were wiped with dilute HCl (10%) and dried with cleanroom wipers. All collectors used nylon netting; the netting for the Hg samplers was thoroughly cleaned and leachate from it was free of detectable Hg. All components were stored in polyethylene bags prior to installation. Litter was collected three times, and collections from a specific collector were aggregated over time. The mass samples were transferred from the netting into paper bags. For the Hg samples, both net and sample were collected in polyethylene bags using the dirty hands/clean hands technique (St. Louis et al. 1994). All samples were frozen upon return to the lab.

Hydrologic export

Two sets of upland surface and subsurface runoff plots have been operating in the watershed since 1971 (Verry & Timmons 1982). Surface runoff is collected below the forest floor (organic material on the mineral surface) and subsurface runoff (interflow) is collected at the top of a Bt horizon of low permeability; both types were sampled on an event basis during 1993–1995. Flow of both components is measured by recording gauges. Runoff in the bog was collected from holes excavated with gloved hands in the acrotelm.

Untreated wood platforms prevented compression of the peat near the holes. Flow at the watershed outlet is monitored by a continually recording stream gauge at a v-notch weir. Flow tends to cease for 2–4 months during the winter (December–March), providing a hydroperiod of approximately 8 to 10 months. Grab samples of streamflow for Hg analysis were collected every two weeks during the ice-free (flow) period of 1993–1995. All sampling was done using a modified clean protocol; a single individual used PVC gloves and a teflon ladle. Sample teflon bottles were washed with a portion of the sample before collection. Flow was partitioned between upland surface runoff and interflow and between upland and bog by hydrograph separation (Dr. Dale Nichols, unpublished data), and hydrologic outputs of Hg were based on these data (Kolka 1996).

Pool sizes

Samples were collected to determine size of pools of Hg in the watershed, including forest floor ($n = 5$), surface mineral soil to 25 cm ($n = 5$), organic soil (peat) in the bog at 35 cm depth below hollows ($n = 5$), aspen leaves ($n = 5$) and wood ($n = 2$), and spruce needles ($n = 4$) and wood ($n = 4$). Samples were collected using PVC gloves, and the soil and wood samples excluded material in contact with the metal sampling apparatus. All samples were frozen upon return to the laboratory.

Laboratory analysis

Analyses of water samples were conducted in a cleanroom (Kolka 1996). Mercury was determined by double amalgamation cold vapor atomic fluorescence spectroscopy (CVAFS), similar to the method of Bloom and Crecelius (1983) and U.S. EPA Method 1631 (U.S. Environmental Protection Agency 1992), using a Brooks-Rand Model 3 CVAFS analyzer. Samples were oxidized with bromine monochloride (BrCl), and excess BrCl was reduced by the addition of hydroxylamine hydrochloride (NH_2OH-HCl) prior to analysis. Sample aliquots were added to bubblers, Hg^{+2} was reduced to Hg^0 by $SnCl_2$, and the Hg^0 was collected on the sample gold trap. Mercury concentrations in solution were based on a standard curve developed at the beginning and end of each batch of 12 samples, with correction for the blank for that batch.

Litter collections were separated into leaves, needles, and other material, including bark, twigs, and lichen; mass of each component was determined after oven-drying at 65 °C and data were converted to mass per unit area. Analyses for Hg for litterfall, forest floor, mineral soil, peat, leaves, needles, and wood were conducted in the same laboratory and using the same instrumentation as the water samples (Fleck 1999). All samples for Hg analysis

were freeze-dried and homogenized in a clean room. A subsample was digested with equal volumes of sulfuric and nitric acid overnight. If presence of undigested material in solution was indicated by turbidity, the sample underwent additional digestion by microwave similar to EPA Method 3052 (U.S. Environmental Protection Agency 1999). Mercury in tissue and soil was expressed as concentration on a dry weight basis. Each batch of 12 samples included a standard curve at the beginning and end of the run, and the following minimal set of QA samples: one blank, one duplicate, one spiked sample, and one known standard reference (NIST Standard Reference Material 1515, Apple Leaves).

Numerical analysis

The concentration of each sample type was applied to the appropriate mass or volume within each landscape component. In all cases, uncertainty was mathematically propagated by appropriate formulae for products, sums, and quotients, including covariances where they were significant (Freese 1962). Significance of differences in estimates was determined by one-way analysis of variance. Litterfall data for the upland was extrapolated to an annual basis using information from about 85 km WSW of MEF, where 84% of annual litterfall in aspen stands was collected in autumn and the proportion varied little with site (Perala & Alban 1982). Measured mass of Hg was therefore adjusted by 1.2 to determine annual litterfall. Annual litterfall in bogs at MEF, including S2, has been measured (Grigal et al. 1985), and the mass of litter collected in the bog was 31% of annual litterfall. Measured mass of Hg in litterfall in the bog was therefore adjusted by 3.2 to determine annual litterfall. To determine biomass of the upland forest, the basal area of the tree overstory was measured ($n = 19$ plots) and applied to a regression relating it to biomass for aspen-dominated forests in the Great Lakes region (from on a published data base – Ohmann et al. 1994). Previously reported overstory biomass was used for the bog forest (Grigal et al. 1985).

Results and discussion

Duplicate analysis of 193 open precipitation, throughfall, and stemflow samples had a mean concentration of 37.0 ng L^{-1} and a pooled standard error (SE) of 3.35%. For runoff and streamflow, 120 duplicates provided a mean concentration of 12.5 ng L^{-1} and a SE of 2.3% (Kolka 1996). For all analyses of litter, 99.5% recovery of spikes was achieved and our analyses of reference material averaged 44.8 ng g^{-1} compared to the reference value of 44 ± 4 ng g^{-1}. The relative error of duplicates varied with the litter material;

Table 1. Concentrations of mercury in S2 watershed, Marcell Experimental Forest, Minnesota. Standard error indicated parenthetically.

Component	Upland	Bog	Entire watershed
Rainfall (ng L^{-1})			9.9 (1.2)[1]
Snow (ng L^{-1})	3.2 (0.4)	9.4 (1.4)	3.1 (0.7)[1]
Throughfall (ng L^{-1})	17.5 (1.3)	33.6 (3.6)	
Stemflow (ng L^{-1})	31.2 (3.1)	113 (22)	
Litterfall – leaves/needles (ng g^{-1})	38.3 (1.4)	29.7 (2.4)	
Litterfall – other (ng g^{-1})	34.3 (6.9)	126 (19)	
Overstory stemwood (ng g^{-1})	1.6 (0.3)	4.9 (0.8)	
Overstory foliage (ng g^{-1})	21.0 (1.2)	21.5 (3.4)	
Forest floor (ng g^{-1})	84.2 (7.5)		
Mineral soil/peat (ng g^{-1})	17.9 (1.9)	44.5 (8.1)	
Runoff (ng L^{-1})	20.6 (1.8)	12.9 (2.2)	
Streamwater (ng L^{-1})			15.1 (1.7)
Groundwater (ng L^{-1})			0.9 (0.2)

[1] Collected in the open.

needles had a mean coefficient of variation (CV) of 9.5%, deciduous leaves of 5.7%, and other material of 15%.

Concentration of Hg in rainfall was 9.9 ng L^{-1} (Table 1), well within the wide range in the literature (St. Louis et al. 1994). The IVL collector in the open and the NADP collector measured nearly identical annual wet Hg deposition in 1995 (6.50 μg m^{-2} and 6.52 μg m^{-2}, respectively) (Kolka 1996; Kolka et al. 1999a), similar to that measured in Michigan, U.S.A. (5.8–9.1 μg m^{-2}; Hoyer et al. 1995), Wisconsin, U.S.A. (6.8–8.7 μg m^{-2}; Fitzgerald et al. 1991), and Finland (6–11 μg m^{-2}; Mukherjee et al. 1995). Throughfall and stemflow (TF-SF) had two to ten times higher concentrations of Hg than rainfall (Table 1), so that hydrologic inputs via TF-SF were 1.5 times higher in the upland and three times higher in the bog than in the open, both significant (Table 2). Twice as much Hg was deposited via TF-SF over the entire watershed than in the open in 1995 (Table 2) (13.0 vs. 6.5 μg m^{-2} – prob. < 0.01). This is a greater difference than that reported for coniferous forests in Sweden (50%, Munthe et al. 1995) and deciduous forests in Tennessee, U.S.A. (43%, Lindberg et al. 1994).

Litterfall was considered a flux of Hg from the atmosphere rather than a recycling from root uptake (Fleck et al. 1999; Guentzel 1997; Iverfeldt 1991; Johnson & Lindberg 1995). Sampling captured peak litterfall; 44% of the litterfall from the upland and 20% from the bog was collected during the first

Table 2. Mercury flux and pool sizes of S2 watershed, Marcell Experimental Forest, Minnesota. Standard error indicated parenthetically.

Component	Upland (μg m^{-2})	Bog (μg m^{-2})	Entire watershed (μg m^{-2})
Precipitation input (yr^{-1})			6.5 (0.22)
Throughfall and stemflow (yr^{-1})	9.75 (0.32)	19.6 (0.84)	13.0 (0.35)
Litter input (yr^{-1})	12.5 (0.85)	11.7 (1.36)	12.3 (0.73)
Overstory	21 (3)	58 (8)	33 (3)
Soil	5250 (520)	3900 (100)	4800 (350)
Hydrologic output (yr^{-1})	2.21 (0.37)	4.04 (0.42)	2.81 (0.28)
Input – output (yr^{-1})	20.1 (1.0)	27.3 (1.7)	22.5 (0.8)

period (8 August to 3 October); 52% and 60% during the second period (3 October to 14 October), and 4% and 20% during the third period (14 October to 15 November). Although leaf litterfall in the upland had a significantly higher Hg concentration than needlefall in the bog (Table 1) (prob. = 0.04), the other component of miscellaneous material was much higher in the bog (Table 1) (prob. = 0.01), probably because of the additions of spruce bark (Pang 1997). Because of the compensating concentrations, inputs of Hg via litterfall were not significantly different between the upland and bog (Table 2) (prob. = 0.64), and were not different over the entire watershed than Hg deposition via TF-SF (Table 2) (12.3 μg m^{-2} yr^{-1} in litterfall vs. 13.0 μg m^{-2} yr^{-1} in TF-SF, prob. = 0.43). When litterfall is considered in studies of Hg flux, an approximate equality with inputs via TF-SF is commonly observed (Guentzel 1997; Iverfeldt 1991). Although this assumption appears valid for the S2 watershed as a whole, it is not valid for either of the individual landscape components. Whereas inputs of Hg via TF-SF were only 80% of litter inputs in the upland (prob. = 0.04), they were about 150% of those inputs in the bog (prob. < 0.01) (Table 2). Canopy structure clearly plays a major role in both kinds of inputs. The input of Hg in litterfall was about half that estimated by Iverfeldt (1991), 25 μg m^{-2} yr^{-1}, and similar to that reported by Munthe et al. (1995) in Sweden, 10.4 μg m^{-2} yr^{-1}, although the latter result was only for five months.

Accurate and precise determination of the pools of Hg in the watershed, and especially in the soil in the upland and the peat in the bog, require detailed sampling and analysis. That effort was not made because the pools were expected to be larger than the fluxes and their relative magnitudes would be sufficient for comparison. The concentration of Hg in aspen wood (1.6

ng g^{-1}) (Table 1) was not different than that reported by Pang (1997) (2.0 ng g^{-1}) (prob. = 0.65), and was applied to the upland overstory stemwood. Leaf concentration has not been reported for aspen, although the concentration (21.0 ng g^{-1}) (Table 1) was similar to that reported for sugar maple, an associated deciduous broadleaf species (24.2 ng g^{-1} – Rasmussen 1994). The measured concentration was applied to the upland leaf biomass. The Hg concentration in black spruce wood (4.9 ng g^{-1}) (Table 1) was lower than that reported by either Moore et al. (1995 – 10 ng g^{-1}) or Zhang et al. (1995a – 20 ng g^{-1}). It was similar, however, to that reported for wood of other conifers, including red pine (3.8 ng g^{-1} – Fleck et al. 1999) and mixed conifers (5.8 ng g^{-1} – Pang 1997). Concentration of Hg in black spruce needles (21.5 ng g^{-1}) (Table 1) was similar to those reported in Ontario (27 ng g^{-1} – Heyes et al. 1998; 15 ng g^{-1} – Moore et al. 1995) and Quebec (ca. 23 to 34 ng g^{-1} – Zhang et al. 1995b). Measured concentrations of spruce wood and needles were applied to the appropriate biomass in the bog.

The concentrations and mass of Hg in soil had high uncertainty because of the limited number of samples. The concentration of Hg in forest floor (84.2 ng g^{-1}) (Table 1) was not significantly different from that based on a regression using forest type, geographic zone, and silt plus clay in the surface soil as independent variables (data from forests across the Great Lakes states from Nater and Grigal (1992) – 102.8 ng g^{-1}, prob. = 0.48). Similarly, Hg mass in forest floor was lower but not significantly different from that based on a regression with the same independent variables (690 μg m^{-2} compared to 844 μg m^{-2}, prob. = 0.58). Concentration and mass of Hg in the surface 25 cm of mineral soil were also lower than estimated (17.9 ng g^{-1} versus 19.5 ng g^{-1}, 4550 μg m^{-2} versus 4950 μg m^{-2}), but in neither case were differences significant (prob. = 0.74, 0.78). The sum of Hg in forest floor and surface soil (5250 μg m^{-2}) (Table 2) was similarly lower, but not significantly, than estimated (5790 μg m^{-2}, prob. = 0.68). Sum of Hg was slightly lower than that for sampled red pine stands in Minnesota (Fleck et al. 1999, 5540 μg m^{-2}), but higher than that for deciduous forests on sandy soils in east-central Minnesota (Grigal et al. 1994, 4020 μg m^{-2}). It was similarly in the range of reports from Sweden (5600 μg m^{-2} in forest floor and upper 30 cm of mineral soil – Lindqvist et al. 1991, 6600 μg m^{-2} in forest floor and upper 40 cm of mineral soil – Aastrup et al. 1991).

Estimation of mass of Hg in the peat soils of the bog requires detailed measurement of both Hg concentration and bulk density with depth (Benoit et al. 1994). Measured Hg concentrations from a single depth are difficult to extrapolate to other depths or to other sites. Detailed data are available from Arlberg Bog, a peatland floristically very similar to the bog in S2 and located about 100 km southeast of MEF (Benoit et al. 1994). The Hg concentration

in S2 peat (44.5 ng g^{-1}) (Table 1) is lower than that reported at a similar depth from Arlberg Bog (approximately 75 ng g^{-1} – Benoit et al. 1994), but is well within the range found at that depth in other peatlands (Jensen & Jensen 1991). A more meaningful comparison among peatlands is the rate of accumulation of Hg, a function of Hg concentration, bulk density, and rate of peat accumulation. The peat samples collected at 35 cm in S2 accumulated before human settlement in the area, about 1895 (Urban & Eisenreich 1988). Computed accumulation rates of Hg in S2 during that period were 6.8 μg m^{-2} yr^{-1}, almost exactly equal to those reported for Arlberg Bog for the same period (7.0 μg m^{-2} yr^{-1} – Benoit et al. 1994), and within the range for the same period in Scandinavia (4 to 12 μg m^{-2} yr^{-1} – Jensen & Jensen 1991). Because of the proximity, floristic similarity, and similarity in rates of pre-industrial Hg accumulation, Arlberg Bog was considered to be a reasonable analog to the bog in S2. The mass of Hg within the surface 50 cm of peat in Arlberg Bog, accumulated since 1750, is 3880 μg m^{-2} (Benoit et al. 1994). That is comparable to other reports of Hg in peatlands in the midcontinent, including an average of 3900 μg m^{-2} per 50 cm from less-detailed sampling of 12 peatlands in northern Minnesota (Grigal & Nord 1983) and 3530 μg m^{-2} per 50 cm from the Experimental Lakes Area of northwestern Ontario, linearly interpolated from total depth and Hg mass (Moore et al. 1995).

Although concentrations of Hg in runoff from the upland were higher than from the bog (Table 1 – prob. = 0.05), hydrologic flux of Hg from the upland was only about half that from the bog (Table 2 – prob. = 0.03), primarily because of greater volume of runoff from the bog. The hydrologic flux of Hg from the watershed, 2.8 μg m^{-2} yr^{-1} (Table 2), is comparable to other reports from forested systems, although measurement techniques differ (1.4 μg m^{-2} yr^{-1} – Lee et al. 1995; 1.5 μg m^{-2} yr^{-1} – St. Louis et al. 1996; 3.4 μg m^{-2} yr^{-1} – Aastrup et al. 1991; 1 to 8 μg m^{-2} yr^{-1} – Meili 1991). The Hg flux from S2 also falls very near that predicted from its proportion of wetland and upland, based on data from a range of watersheds in Wisconsin, U.S.A., with varying wetland areas (3.4 μg m^{-2} yr^{-1} – Babiarz et al. 1998). Flux of Hg from S2 is also very similar to the post-industrial Hg contribution from the terrestrial portion of watersheds to lakes, based on sediment analyses of seven lakes near MEF in northern Minnesota (Swain et al. 1992). That flux, 3.3 μg m^{-2} of terrestrial area yr^{-1}, is within the 95% confidence interval of our measurement (2.2 to 3.4 μg m^{-2}).

Evaluating the Hg budget for S2 in units of mass per unit area empha-sizes differences in processes between the two landscape components. The resultant of those processes on the Hg budget of the entire watershed, however, depends on the area of each component. Although input of Hg by TF-SF was much higher per unit area in the bog than in the upland (Table
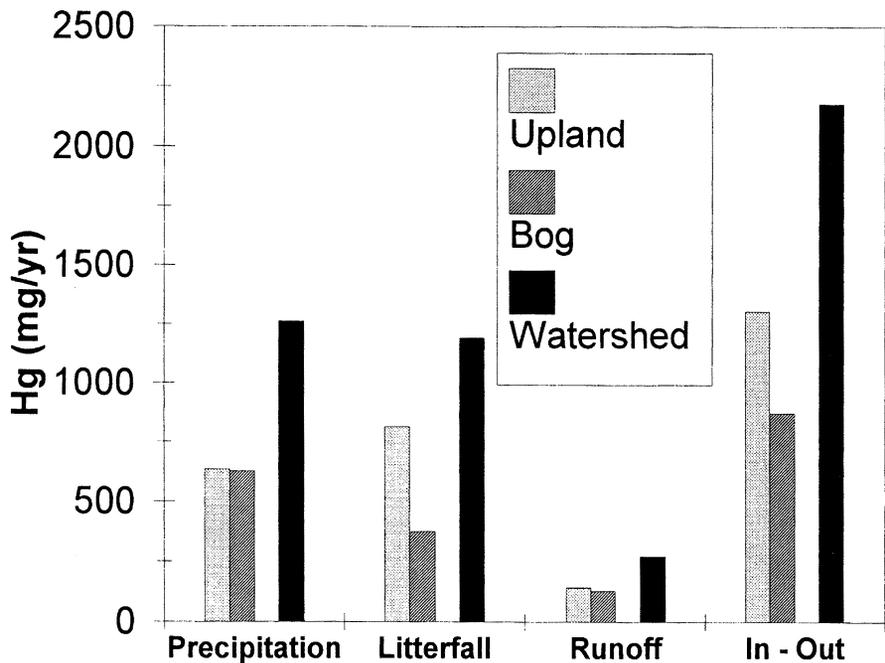
Figure 1. Inputs and outputs of Hg into a forested upland/peatland watershed in northern Minnesota. The upland portion of the watershed covers 6.5 ha, and the bog (peatland) 3.2 ha.

2), the contribution of each landscape component to total deposition of Hg to the watershed was nearly equal (Figure 1). Small differences in Hg input per unit area via litterfall (Table 2) were further magnified when the area of each landscape component was considered, so that upland litterfall contributed more than twice as much Hg to the watershed than did bog litterfall (Figure 1). Loss of Hg via runoff was also nearly equal for each of the landscape components (Figure 1).

The estimated pool size of Hg in the overstory is marginally greater than the annual inputs of Hg (prob. = 0.07) and much greater than outputs (prob. <0.01) (Table 2). Both inputs and outputs are more than two orders of magnitude smaller than the pool in the soil (Table 2). The difference between measured inputs and outputs indicates a sizeable net sink of Hg in both upland and bog (Table 2). The size of the sink in the bog, 27.3 μg m^{-2} yr^{-1} (Table 2), is within the confidence interval of the recent rate of Hg accumulation reported for Arlberg bog (24.5±7.9 μg m^{-2} yr^{-1}) (Benoit et al. 1994). The explanation of the sink in the upland, 20 μg Hg m^{-2} yr^{-1} (Table 2), is more uncertain. Even if only the Hg deposition actually measured in litterfall on the upland is considered, disregarding the extrapolation to an annual basis, a substantial unexplained difference of about 18 μg Hg m^{-2} yr^{-1} remains.

Deep leaching to groundwater is an unlikely pathway of loss (Johnson & Lindberg 1995). Concentrations of Hg in groundwater on the MEF are about 1 ng Hg L^{-1} (Table 1, J. Fleck, unpublished data), lower than those reported in northern Wisconsin (2.8 ng Hg L^{-1} – Krabbenhoft & Babiarz 1992). If all Hg in groundwater were derived from surface processes, the hydrologic flux to groundwater in northern Minnesota (20 to 30 cm H_2O yr^{-1}) would only provide a sink of about 2.5 μg Hg m^{-2} yr^{-1}, far short of the size of the sink in the upland.

A possible explanation for this difference between inputs and outputs is simply Hg accumulation in the soil (Aastrup et al. 1991; Hultberg et al. 1995; Lindqvist et al. 1991). We have estimated mass of Hg in forest floor and mineral soil of the upland to be 5250 μg Hg m^{-2} (Table 2), and annual changes in this pool at the rate implied by the unexplained difference would be less than 0.5% yr^{-1}, virtually impossible to measure. Differences can also be considered over the longer term. Before 1850, estimated atmospheric Hg deposition to the surface of lakes in the region, based on accumulation in sediments of lakes that occupy a large proportion of their watersheds, was 3.7 μg m^{-2} yr^{-1} (Swain et al. 1992), and net accumulation in nearby Arlberg Bog was 7 μg m^{-2} yr^{-1} (Benoit et al. 1994). The higher accumulation and hence inferred higher deposition to the bog is reasonable if deposition to terrestrial surfaces is enhanced because of the presence of vegetation. Current rates of accumulation in both lakes and bogs are about 3.5 times higher than pre-industrial rates (Benoit et al. 1994; Swain et al. 1992), with an average of about 18.5 μg m^{-2} yr^{-1} [3.5 × (3.7 + 7)/2], very similar to the annual difference between Hg inputs and outputs in the upland of S2 (Table 2). If soil were wholly accumulating this excess Hg, then from 300 (current rate) to 1000 years (pre-industrial rate) would be required to accumulate the present pool. These accumulations would be in addition to the background levels of Hg derived from the geologic substrate. When considered over the long term, it would appear that a significant unmeasured sink or loss of Hg from the upland must exist or soil levels would be much higher. Many other studies report lower rates of apparent accumulation (e.g., St. Louis et al. 1996 – 2 to 3 μg m^{-2} yr^{-1}), but those rates often do not include litterfall as an input.

The most likely major unmeasured pathway of loss, both historically and at present, is volatilization, whereby Hg^{2+} in soils is converted to Hg^0 by reductive processes and then released to the atmosphere. Although there is strong circumstantial evidence for this process, it has not been thoroughly investigated, due in large part to analytical difficulties (Lindberg et al. 1995). Accurate measurement of surface-to-atmosphere fluxes is difficult but imperative if we are to understand the global cycle of Hg. A similar conclusion regarding the importance of volatilization was reached by Johnson and Lind-

berg (1995). During the pre-industrial period, annual volatilization losses should have approached a steady state with net deposition, ca. 2 to 9 μg m^{-2} yr^{-1}. Based on the higher current annual deposition and concentrations of Hg in soils, it is probable that current volatilization rates are also higher than pre-industrial rates.

Conclusions

A comprehensive budget of a forested upland/peatland watershed indicates that fluxes of Hg from the atmosphere are much higher that measured in open precipitation collectors because of inputs by both washoff of dryfall (as throughfall and stemflow) and litterfall. Pools of Hg in vegetation and especially in soil far exceed annual inputs and outputs. The two landscape components differ significantly in the magnitude of Hg fluxes and pools. Although the inputs, outputs, and accumulation are approximately balanced in the peatland, there appears to be an unmeasured sink of Hg in the upland that is probably related in part to accumulation in soil and in part to volatilization. If that is the case, a significant fraction of the Hg annually deposited on uplands may be returning to the atmosphere.

Acknowledgements

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