

Mercury Cycling and Transport in the Lake Champlain Basin

James B. Shanley, Andrea F. Donlon, Timothy Scherbatskoy, and
Gerald J. Keeler

ABSTRACT

Mercury contamination and its potential effects on human health is an issue of growing concern in the Lake Champlain basin. This paper is an effort to review and synthesize the current state of understanding of sources, sinks, and movement of Hg within the basin. We compile and review existing information and present some new data on Hg concentrations and fluxes in atmospheric deposition, throughfall, foliage, surface water, soil water, soil, and biota, then use these data to formulate a conceptual model of Hg cycling in the basin. Mercury is primarily of anthropogenic origin and enters the basin in atmospheric deposition. At a site near the center of the basin, Hg deposition during a two-year period averaged $444 \text{ mg ha}^{-1} \text{ yr}^{-1}$, of which about 70% was dry deposition. Most of this Hg reaches the land surface in throughfall or litterfall and is retained in the soil. A significant percentage of the Hg may be re-volatilized to the atmosphere. Stream export of Hg averaged only $27 \text{ mg ha}^{-1} \text{ yr}^{-1}$ for the same two-year period. Mercury appears to move to stream channels primarily in association with DOC, whereas Hg in streamwater tends to be associated with organic suspended sediment. Our review identified a need for more research on the speciation and bioaccumulation of mercury, and more research on Hg cycling in non-forested areas of the basin.

INTRODUCTION

Mercury (Hg) contamination of surface waters and biota has emerged as a global problem [Nriagu and Pacyna, 1988; Fitzgerald, 1993; U.S. EPA, 1997]. Concern for mercury contamination in the environment stems from its potent neurotoxicity to humans. Mercury concentrations in fish such as walleye in Lake Champlain are elevated to the point where consumption of greater than 250 g of fish per month exceeds the maximum U.S. EPA recommended Hg dosage. The State of Vermont has issued an advisory on fish consumption that warns of this danger, and cautions children and pregnant women not to consume any walleye, nor any more than 2-3 servings per month of other fish species [State of Vermont, 1990]. A recent study [River Watch Network, 1998] suggests a possible link between neurological disorders among the native Abenaki and consumption of fish from the Missisquoi River. Public health concerns prompted passage of a 1998 law in Vermont to phase in limitations on Hg emissions. Discussion continues among other U.S. state and Canadian provincial leaders to enact similar measures.

On a global basis, Hg is increasing in the environment [Swain *et al.*, 1992; NESCAUM *et al.*, 1998]. Upward trends in Hg have been indicated by sediment cores in Alaska [Engstrom and Swain, 1997], an increase in Hg in air over the North Atlantic Ocean between 1977 and 1990 [Slemr and Langer, 1992], and as described throughout the global biogeochemical Hg cycle by Fitzgerald *et al.* [1998]. Localized areas, however, have undergone recent declines in Hg. Engstrom and Swain [1997] used sediment cores from eastern Minnesota lakes to demonstrate that Hg deposition increased between 1920 and 1960, but decreased after 1960. They suggested that the Hg decrease in their midwestern sites may represent a decrease in Hg emissions in the industrial areas of eastern North America.

In the Lake Champlain basin, as in many areas of North America, the primary Hg source is emissions from anthropogenic activity, primarily from coal combustion and waste incineration, and subsequent wet or dry deposition to the landscape [Watzin, 1992;

In press

for AGU monograph
on Lake Champlain
and its basin

(American Geophysical
Union)

Expected publication

April 1999

Vasu and McCullough, 1994; Scherbatskoy *et al.*, 1997]. Industrial and geologic inputs of Hg to Lake Champlain basin waters are minor. Although most of the Hg deposited in the Lake Champlain basin probably originates from outside the basin, there is growing evidence to suggest that local industry and waste incineration as well as emission of Hg from vegetation, soils, landfills, and land-applied sludge contributes up to half of the total deposition [NESCAUM *et al.*, 1998].

The Lake Champlain basin has a large forested land area that has the potential to capture atmospheric pollutants and transfer them to soils, surface waters, and groundwater by several mechanisms. Terrestrial ecosystems accumulate atmospheric pollutants through wet and dry deposition, throughfall (precipitation passing through the forest canopy), litterfall (deposition of senescent foliage), and interception of cloud water in higher elevations. Forest canopies in this region have foliar surface areas up to 4.6 times greater than the land area they cover [Rea *et al.*, 1996], providing Hg concentration in throughfall that averages twice that of precipitation and an annual Hg flux in litterfall that is greater than annual wet deposition [Rea *et al.*, 1996]. Swain *et al.* [1992] showed the importance of watershed:lake area ratio in Hg loading to lake sediments. Examining the behavior of Hg in forested catchments, therefore, is important to understanding the present and long-term role of atmospheric Hg in the Lake Champlain basin.

From a human health perspective, it is the concentration of methylmercury (Me-Hg) that is critical because this form bioaccumulates in fish and is toxic to humans. In aquatic systems, Me-Hg is generally present at concentrations only 1 to 10% of total Hg concentration [Lee and Iverfeldt, 1991; Driscoll *et al.*, 1994; U.S. EPA, 1997]. However, Me-Hg can comprise a greater percentage in organisms. Mason and Sullivan [1997] found in Lake Michigan that by the third trophic level, all Hg in aquatic organisms was Me-Hg. Water column Me-Hg is a result of methylation of ionic Hg which occurs in sediment and the water column by microbial action and abiotic processes. Methylation rates increase under anaerobic conditions [Branfireun *et al.*, 1996], high DOC [Miskimmin *et al.*, 1992], warm temperatures, and low pH [U. S. EPA, 1997]. Wetlands tend to be sources of Me-Hg [Kelly *et al.*, 1995; Krabbenhoft *et al.*, 1995; Branfireun *et al.*, 1996].

The objectives of this paper are to summarize the somewhat disparate information on Hg pools, concentrations, and fluxes in waters, sediments, and biota in the Lake Champlain basin. We will draw on monitoring data and research results from a deposition station and catchment monitoring site near the center of the basin, as well as data from other relevant studies and monitoring efforts. We will synthesize the available information into an overview of Hg cycling in the Lake Champlain basin. Based on this assessment we will identify gaps in information and understanding and suggest directions for further research.

METHODS

The Lake Champlain basin comprises 21,150 km², including much of western Vermont, northeastern New York, and part of southern Québec (Figure 1). The ratio of land to lake surface area in the basin is 19:1. Land cover is 64% forest, 16% agricultural, 14% water/wetlands, and 6% urban/developed [personal communication, Eric Pyle, Vermont Center for Geographic Information]. The largest population centers in the basin are Burlington and Rutland, Vermont and Plattsburgh, New York. The topography is generally mountainous, with peaks exceeding 1500 m in the Adirondack Mountains of New York and 1300 m in the Green Mountains of Vermont. Agricultural activity is concentrated in the gently sloping lands around the shores of Lake Champlain. Despite its rural character, the area receives pollutants transported from the industrial midwest via prevailing westerly winds [Scherbatskoy *et al.*, this volume; Olmez *et al.*, 1998]. With respect to Hg, however, anthropogenic sources from within the region appear to be more important than sources from outside the northeast (61% and 39%, respectively) [NESCAUM *et al.*, 1998].

This paper draws extensively from research at the Proctor Maple Research Center (PMRC) and the Nettle Brook catchment, both in Underhill Center, Vermont, 34 km east

of Lake Champlain (Figure 1). We summarize and update the deposition and streamflow record discussed in two earlier papers [Scherbatskoy *et al.*, 1997; Scherbatskoy *et al.*, 1998]. We also report on results from other headwater streams and larger rivers in the Lake Champlain basin, and present new data on Hg in soils, soil water, and plankton. Information for this paper has also been assembled from reports of the Vermont Agency of Natural Resources, U.S. Geological Survey, and other publications. The remainder of this section provides background information and methods for previously unpublished data newly presented in this paper.

PMRC and the Nettle Brook catchment are on the western slope of Mt. Mansfield. The sites are operated by the Vermont Forest Ecosystem Monitoring program (VForEM) as part of their long-term integrated studies on responses of forested ecosystems to environmental change [Wilmot and Scherbatskoy, 1994]. PMRC, at an elevation of 400 m, has a 30-m tower and a full meteorological station. Since 1991, wet Hg deposition has been determined daily and dry deposition weekly, as described in Landis and Keeler [1997]. PMRC is the only site in the Lake Champlain basin where Hg deposition is routinely monitored.

Nettle Brook is an 11-ha mixed hardwoods catchment 3 km southeast of PMRC. Elevation ranges from 445 to 664 m, aspect is southwest, and slope averages 35% (range 5-75%). Soils are moderately well-drained Peru extremely stony loam underlain by mica-albite-quartz schist bedrock. Average annual rainfall is 1100 mm. January daily minimum temperature is -16C and July daily maximum temperature is 24C. Annual sulfate and nitrate deposition averages 21 and 16 kg ha⁻¹, respectively [Scherbatskoy *et al.*, 1998]. Nettle Brook is the only site in the basin where streamwater Hg is regularly monitored and Hg biogeochemical process research is conducted [Scherbatskoy *et al.*, 1998]. Since October 1993, stream water samples have been collected at Nettle Brook at a continuously gauged V-notch weir for analysis of Hg, DOC, and suspended sediment. Sampling frequency has varied, with higher priority given to high-flow periods, particularly the snowmelt periods of 1994, 1995, and 1996. In total, 106 samples were collected between October 1993 and November 1997.

Additional Hg determinations have been made at PMRC and in the Nettle Brook watershed. During the 1994 snowmelt, meltwater was collected daily at PMRC from a 1-m² Teflon-coated lysimeter installed on the ground beneath the snowpack [Scherbatskoy *et al.*, 1997]. In 1997, soil water was collected from the O-horizon and B-horizon at 2 sites along Nettle Brook using non-tension fiberglass wick collectors. In December, 1997, soil samples were collected using a soil corer at 3 depths (20, 300, and 500 mm) at PMRC and at 2 depths (60-100 mm and 220-280 mm) from soil water sampling areas in the Nettle Brook area. Soil sample collection and analysis methods are described in Rea [1998]. Stream, snowmelt, and soil water samples were collected in acid-cleaned, triple-bagged Teflon bottles. Particle-free gloves were worn during sample collection.

Additional samples have occasionally been collected from four other sites, one headwater stream and three river sites, in the Lamoille River drainage basin (Figure 1). The headwater stream, Stream 10, drains a mixed conifer and hardwoods watershed between 775 and 1180 m elevation in Mt. Mansfield State Park. The stream originates near the Nose portion of the summit ridge of Mt. Mansfield and descends steeply down the west face. Of the three river sites, one sampling site was on the lower Browns River downstream of Nettle Brook, and two were on the Lamoille River, one upstream of the Browns River in Jeffersonville and the other near Lake Champlain at the walleye spring spawning grounds in Milton (Figure 1). Samples from these sites were collected by submerging the sample bottles 30 cm below the water surface approximately 1.0 to 1.5 m from the river bank. Sample bottles were extended into the river using a custom-made pole sampler constructed with a PVC pipe end and a broom handle, with all non-PVC parts wrapped in Teflon tape.

Samples were shipped by overnight courier to the University of Michigan Air Quality Laboratory (UMAQL) in Ann Arbor, MI, where they were analyzed for total and dissolved (<0.22 μm) Hg was performed in a Class 100 ultra-clean laboratory. After arrival at the laboratory, Hg was stabilized until analysis by oxidation in a 1% BrCl solution. For total Hg determination, the oxidized Hg was reduced by NH₂OH and SnCl₂ to elemental Hg, bubbled out of solution in a Hg-free nitrogen gas stream, and captured

onto a gold-coated bead trap. Mercury was then thermally desorbed from the trap in a Hg-free helium gas stream and quantified by cold vapor fluorescence spectrometry. Analytical and quality assurance details are given in Scherbatskoy *et al.* [1998]. No Hg speciation was performed. The DOC (0.7 μm filtered) and suspended sediment determinations are described by Scherbatskoy *et al.* [1998]. Stream Hg flux at Nettle Brook was calculated using a concentration/discharge relation as described in Scherbatskoy *et al.* [1998].

On August 27, 1997, six plankton samples and three water samples were collected from Mallets Bay near the mouth of the Lamoille River. Three plankton samples were collected in acid-washed, triple bagged 7-ml Teflon vials in each of two net sizes, 63 μm and 202 μm . Plankton samples were stored in a freezer for one month, then ground with acid-cleaned borosilicate glass Duall tissue grinders in a portable HEPA clean chamber at PMRC. Water samples were collected using the pole sampler described above. Particle-free gloves were worn at all times when collecting and handling samples. Water and plankton samples were sent on ice via overnight courier to the University of Wisconsin water laboratory for analysis of total Hg and Me-Hg as described in Back *et al.* [1995].

RESULTS

In this section we have compiled available published information as well as previously unpublished data on Hg concentrations, pools, and fluxes in the Lake Champlain basin. The Hg record at Nettle Brook for March 1994 through February 1996 as reported in Scherbatskoy *et al.* [1998] is updated to include the 1996 and 1997 snowmelts and several rain events during the summer of 1997. We also report new data on Hg concentrations in soil water, soil, and plankton.

Hg in Atmospheric Deposition

Mercury emissions to the atmosphere generally occur in three forms: gaseous elemental Hg (Hg^0 (g)), gaseous divalent Hg (Hg(II) (g)), and particulate Hg. Gaseous elemental Hg is relatively insoluble and is not susceptible to wet or dry deposition. It can travel long distances and has an atmospheric residence time of one-half to two years. Because of its long residence time, Hg^0 (g) is the most prevalent form of Hg in the atmosphere. Gaseous divalent Hg is subject to rapid dry or wet deposition, as are particulate forms of Hg. Deposition of Hg(II) (g), wet divalent Hg (Hg(II) (aq)), and particulate forms of Hg occurs close to their source, with a typical residence time in the atmosphere of hours to weeks [U. S. EPA, 1997; NESCAUM *et al.*, 1998]. When re-deposited, these forms of Hg are commonly quantified in dry deposition (vapor or particulate phase) and wet deposition (precipitation).

At PMRC, total atmospheric Hg deposition was 425 and 463 mg ha^{-1} for 2 years beginning March 1994 (Table 1) [Scherbatskoy *et al.*, 1998]. Of this total, dry deposition accounted for most of the Hg flux, with only 75 and 93 mg ha^{-1} as wet deposition. Dry deposition was calculated by the "big leaf" model given in Scherbatskoy *et al.* [1997] as amended by Lindberg [1993]. Vapor phase Hg (mostly Hg^0 (g) and some Hg(II) (g)) dominates dry deposition [Rea, 1998] and occurs at a relatively constant concentration of approximately 2 ng m^{-3} throughout the year, with a slight increase in the summer months because of greater deposition velocities [Scherbatskoy, 1997]. Wet deposition of Hg also tends to be greatest in the summer primarily due to higher Hg concentrations in precipitation. This pattern has been observed in other studies [Lindberg *et al.*, 1992; Hoyer, 1995], but no causes have been identified [Scherbatskoy *et al.*, 1997]. Wet Hg deposition at the PMRC site is similar in magnitude and seasonal pattern to sites in rural northern Michigan [Hoyer *et al.*, 1995; Keeler *et al.*, 1995; Rea, 1998].

Hg in Surface Water

Total Hg (Hg_T) concentrations in surface waters within the Lake Champlain basin ranged from 0.1 to 80 $ng L^{-1}$ [Scherbatskoy *et al.*, 1997; 1998] (Figure 2). Median Hg_T concentrations at each site generally ranged from 2 to 5 $ng L^{-1}$, but all sites had occurrences of $>5 ng L^{-1} Hg_T$. At Nettle Brook, Hg_T concentrations ranged from 0.1 to 79.7 $ng L^{-1}$ ($n=106$, median 2.1 $ng L^{-1}$) (Figure 3). Dissolved Hg (Hg_D) concentrations in Nettle Brook streamwater ranged from 0.1 to 3.5 $ng L^{-1}$ ($n=106$, median 1.4 $ng L^{-1}$). The low but consistent Hg_D concentrations account for about 33% of the annual Hg flux at Nettle Brook [Scherbatskoy *et al.*, 1998]. Most of the remaining 67% of the annual Hg export in streamwater occurred as particulate Hg during brief periods in extreme hydrologic events [Scherbatskoy *et al.*, 1998]. The total Hg flux for the two years beginning March 1994 was 32 and 22 $mg ha^{-1} yr^{-1}$ respectively.

Total Hg concentrations at Nettle Brook in 28 samples collected subsequent to the study of Scherbatskoy *et al.* [1998] did not exceed 10 $ng L^{-1}$. Some of these samples from summer storms represent the first non-snowmelt high flows sampled at Nettle Brook. Total Hg concentrations during these storms were only somewhat above typical baseflow concentrations; the highest Hg_T concentration observed in 1997 (9.3 $ng L^{-1}$) occurred during the event with the highest peak flow of that year (Figure 3). Although peak flows were in excess of 3.5 $mm hr^{-1}$ in the 1996 melt and 2.0 $mm hr^{-1}$ in the 1997 summer storm, flows at the time of sampling were considerably lower. The new data did not change the concentration-discharge relation (Figure 4) used to calculate stream Hg flux as described in Scherbatskoy *et al.* [1998].

Mercury concentration ranges and temporal dynamics at downstream sites on larger streams mimicked those at the headwater sites. Based on synoptic sampling at 3 sites downstream of Nettle Brook within the Lamoille River watershed in 1994-1997 ($n=13$ at each site), Hg_T concentrations ranged from 0.7 to 52.6 $ng L^{-1}$ (median 3.0 $ng L^{-1}$), while Hg_D ranged from 0.5 to 5.1 $ng L^{-1}$ (median 1.3 $ng L^{-1}$). There was significant seasonal variation in Hg concentration due to spring snowmelt or flooding summer rains. Under base flow conditions, total Hg concentrations were 2-3 $ng L^{-1}$ (except for one outlier of 12 $ng L^{-1}$), with approximately 50% of the Hg_T as Hg_D . During the flood of 7 August, 1995, however, Hg_T concentration at the Milton site, furthest downstream near the mouth of the Lamoille River at Lake Champlain, attained 52.6 $ng L^{-1}$ (Figure 5), while Hg_D increased only slightly.

Total Hg in Lake Champlain lakewater ranged from $\sim 1 ng L^{-1}$ at a shallow site in Mallets Bay [T. Scherbatskoy, A. Donlon, and M. Watzin, University of Vermont, unpublished data] to 8 $ng L^{-1}$ (median $\sim 3 ng L^{-1}$) in the deep-water lake 1.6 km west of Burlington [Cleckner *et al.*, 1995] (Figure 2).

Other Hg Determinations

Snowpack and snowmelt. Only one determination of Hg in the snowpack was made; 1.8 $ng L^{-1}$ in March 1994 [Scherbatskoy *et al.*, 1997]. Mercury in snow meltwater, also in 1994, ranged from 2 to 9. $ng L^{-1}$ and averaged 4.8 $ng L^{-1}$ [Scherbatskoy *et al.*, 1998]. Haines *et al.* [1995] measured 3.5 $ng L^{-1}$ in the snowpack at a Vermont site just outside the Lake Champlain basin.

Throughfall. Throughfall was collected at PMRC in Underhill Center, VT during August and September of 1994 [Rea *et al.*, 1996]. The mean volume-weighted Hg concentration was $12.0 \pm 8.5 ng L^{-1}$ with a range of 4.5 to 35.8 $ng L^{-1}$. Net throughfall for 2 months was 12 $mg ha^{-1}$ [Rea *et al.*, 1996].

Foliage. Rea [1998] found that Hg concentration consistently increased in foliage throughout the growing season and peaked in litterfall. In 1995, foliar Hg concentration increased from $3.6 \pm 2.6 ng g^{-1}$ at budbreak to $28.8 \pm 2.4 ng g^{-1}$ in September foliage to $47.1 \pm 5.6 ng g^{-1}$ in October litterfall [Rea, 1998]. In 1994, Hg increased from 34.2 ± 7.2

ng g⁻¹ in August foliage to 53.2 ± 11.4 ng g⁻¹ in October litterfall [Rea *et al.*, 1996]. The total flux of Hg from the canopy (throughfall + litterfall) was attributed primarily to dry deposition and was ~2 times the flux from precipitation [Rea *et al.*, 1996].

Litterfall. Mercury in litterfall in the fall of 1996 represented an annual areal Hg flux of 158 mg ha⁻¹ yr⁻¹ [Rea, 1998].

Soils. Mercury concentrations in soils from PMRC [Rea, 1998], at Nettle Brook, and Stream 10 [A. Donlon, unpublished data] agreed very closely. The Oa horizon had 210 ng g⁻¹ (n=3) at PMRC, 204 ng g⁻¹ (n=3) at Nettle Brook, and 169 ng g⁻¹ (n=1) at Stream 10. The B horizon had 70 ng g⁻¹ (n=3) at PMRC, 58 ng g⁻¹ (n=4) at Nettle Brook, and 75 ng g⁻¹ (n=2) at Stream 10 (Figure 6).

Soil water. Between April and November, 1997, soil water was sampled at two sites along Nettle Brook and one site along Stream 10 using non-tension fiberglass wick collectors. Soil water at the middle elevation location along Nettle Brook had an average total Hg concentration of 20.1 ng L⁻¹ (n=13) just below the Oa soil horizon and 3.0 ng L⁻¹ (n=4) within the B horizon (Figure 6). Concentrations at an upper elevation location near the headwaters of Nettle Brook averaged 3.5 ng L⁻¹ (n=9) below the Oa horizon and 1.1 ng L⁻¹ (n=10) within the B horizon. The upper elevation site at Nettle Brook is located on a wet hillslope, and its consistently low Hg concentrations may reflect the chemistry of discharging groundwater rather than soil water. At Stream 10, the average Hg concentration was 16.6 ng L⁻¹ (n=6) just below the Oa soil horizon and 6.6 ng L⁻¹ (n=4) within the B horizon.

Mercury and DOC concentrations were positively correlated at all sites. DOC concentrations at the middle site at Nettle Brook averaged 22.7 mg L⁻¹ (n=12) and 2.39 mg L⁻¹ (n=2) at the Oa and B horizons, respectively. By contrast, DOC concentrations at the upper site averaged only 2.53 mg L⁻¹ (n=8) and 0.55 mg L⁻¹ (n=8) at the two depths, respectively. DOC in soil water at Stream 10 was 18.8 mg L⁻¹ (n=6) below the Oa horizon and 11.25 mg L⁻¹ (n=3) in the B horizon.

Sediments. Two surveys of Hg in sediments were conducted in the basin in the early 1990's: a survey of Hg in stream sediments by the USGS [Colman and Clark, 1994] and a survey of Hg in lake bottom sediments [MacIntosh, 1994] (Table 2). In each survey, the median Hg concentration was near 200 ng g⁻¹. At six sites where sampling locations approximately coincided in the 2 studies, near stream outlets to the lake, Hg concentrations agreed closely (r²=0.67).

Plankton. In 1997 Hg and Me-Hg (dry weight) concentrations were determined in plankton from Lake Champlain waters [T. Scherbatskoy, A. Donlon, and M. Watzin, University of Vermont, unpublished data]. Mercury concentration averaged 410 ± 110 ng g⁻¹ and 760 ± 20 ng g⁻¹ in 3 samples each of small (between 63 and 202 μm) and large (>202 μm) plankton, respectively. Corresponding Me-Hg concentrations were 5 ± 3 ng g⁻¹ for small plankton and 21 ± 3 ng g⁻¹ for large plankton.

Fish. A compilation of Hg concentrations in fish tissue in the Lake Champlain basin from 1970 to present is available from the Vermont Agency of Natural Resources (VANR) and other government sources in Vermont, New York, and Québec, and the University of Vermont [State of Vermont, 1990; 1997]. The highest concentrations are typically found in walleye, but elevated Hg occurs consistently in lake trout, smallmouth bass, and northern pike, and frequently in largemouth bass, yellow perch, and pickerel. Higher Hg concentrations in fish are favored in acidic and brownwater lakes [State of Vermont, 1997]. Mercury is detectable (>50 ng g⁻¹) in virtually all fish tissue analyzed. Mercury concentration is typically greater than 500 to as much as 2000 ng g⁻¹ for walleye. Mercury concentration for brown bullhead and trout other than lake trout more typically range from 100 to 200 ng g⁻¹. Mercury in walleye in the Missisquoi River averaged 700 ng g⁻¹ in 1970 (n=4) and 990 ng g⁻¹ in 1990 (n=10) [State of Vermont, 1990]. Because Hg concentrations in fish tissue are reported on a wet weight basis, concentrations in fish

are actually considerably higher than those in sediment and plankton, as would be expected from bioaccumulation. While they continue routine monitoring, VANR is collaborating with the New Hampshire Department of Environmental Services and the U.S. EPA on a comprehensive interpretive study on fish/water/sediment Hg and Me-Hg in lakes throughout Vermont and New Hampshire, including 19 lakes within the Lake Champlain basin [N. Kamman, VANR, personal communication].

MERCURY INPUT-OUTPUT BUDGETS

Scherbatskoy *et al.* [1998] determined watershed retention rates for Hg of 92 and 95% in the Nettle Brook catchment for the two years beginning March 1994 (Figure 7). Because of the tendency for episodic transport of Hg, retention may be considerably less than this amount during snowmelt and other high flow periods, and considerably greater than this during base flow periods. The net Hg retention at Nettle Brook (92-95%) is greater than the 80% to 90% retention reported in Sweden [Aastrup *et al.*, 1991; Johanssen *et al.*, 1991]. It is comparable to the 92% retention (an underestimate because dry deposition was not considered) determined by Krabbenhoft *et al.* [1995] at a Wisconsin site.

The Hg retention percentages above are based solely on mass balance considerations. Mercury deposited to the basin that is not exported in streamflow is said to be "retained" in the basin, though in fact much of the atmospheric Hg incident to the basin may be volatilized to the atmosphere, as observed in catchments in Tennessee [Johnson and Lindberg, 1995] and Sweden [Bishop *et al.*, 1998]. Because most of the Hg input is by dry deposition to foliage (Table 1), volatilization may occur directly from foliar surfaces.

A simple extrapolation of the Hg input-output budget from the 11-ha Nettle Brook catchment to the entire Lake Champlain basin may be misleading. The basin as a whole may have a Hg deposition rate somewhat lower than that of Nettle Brook because 36% of the basin area is non-forested land, where the dry deposition rate may be limited by a lower stomatal uptake potential. On the other hand, non-atmospheric anthropogenic sources of Hg may be significant at the larger scale. An estimate of Hg flux from Lake Champlain itself can be made by assuming that the median Hg concentration from a set of samples from the deep part of the lake [Cleckner *et al.*, 1995] approximates the mean annual Hg concentration of lake water. The product of this Hg concentration (3 ng L^{-1}) and the mean annual discharge from the lake [Shanley and Denner, this volume] yields a Hg output of $\sim 15 \text{ mg ha}^{-1} \text{ yr}^{-1}$. This value has a high uncertainty, but the results of this exercise suggest that the Hg retention for the basin as a whole is similar to that of Nettle Brook, i.e. $> 90\%$.

SOURCES OF MERCURY

Atmospheric Hg is the dominant source of Hg to the Lake Champlain basin [NESCAUM *et al.*, 1998]. Atmospheric Hg is in part natural, and in part derived from industrial sources including smelting, fossil fuel combustion, and waste incineration. There is no significant mineralogical source of Hg in the Lake Champlain basin, thus direct geologic contributions of Hg to basin waters from geologic weathering are negligible. Other potential non-atmospheric transfers of Hg to the landscape include leaching of Hg from landfills, discharge of Hg-containing industrial effluent and wastewater treatment plants to streams, and land application of Hg-containing sludge. Also, Hg may have an agricultural source because it was commonly used as an agricultural fungicide prior to the 1970's [Hem, 1985]. Industrial and agricultural sources of Hg are believed to be minor in the Lake Champlain basin.

About half of the Hg deposition in the Lake Champlain basin may be from in-basin sources. NESCAUM *et al.* [1998] used the Regional Lagrangian Model of Air Pollution (RELMAP) to simulate patterns of Hg transport and deposition. The results, which should be regarded as best estimates, suggested that 47% of Hg deposition in the northeast U.S. is attributable to regional sources; 30% to U.S. sources outside the region;

and 23% from the global atmospheric reservoir. About 27% of the modeled Hg deposition originated from utility and non-utility boilers, and more than 50% originated from municipal waste combustion (Figure 8) [NESCAUM *et al.*, 1998]. One of the largest waste incinerators in the basin is a medical waste combustion facility in Colchester, Vermont. In a monitoring check in June 1996, the facility was emitting Hg at the rate of 4 g hr^{-1} [Vermont DEC, 1996]. If extrapolated to an annual rate over the entire basin, this emission equates to $17 \text{ mg ha}^{-1} \text{ yr}^{-1}$, or enough to account for 4% of the deposition in the basin.

TERRESTRIAL PROCESSES

From March 1995 to February 1996, Scherbatskoy *et al.* [1998] determined an annual Hg deposition to the landscape of 463 mg ha^{-1} , of which 370 mg ha^{-1} was dry deposition. Within this period (summer of 1995), Rea [1998] independently determined Hg dry deposition rates of $\sim 200 \text{ mg ha}^{-1} \text{ yr}^{-1}$. A comparable Hg flux of 158 mg ha^{-1} was deposited as litterfall in the Nettle Brook area in 1995 [Rea, 1998]. Rea [1998] concluded that uptake of gaseous Hg through leaf stomata, which represented most of the dry deposition flux, was able to account for the Hg flux in litterfall. A key finding in support of gaseous uptake was the progressive increase in foliar Hg through the growing season. Increases in Hg concentration from rainfall to throughfall, together with the high Hg concentrations in litterfall [Rea *et al.*, 1996], suggest that much of the incident Hg finds its way to the forest floor. Considerable uncertainty remains about processes controlling the cycle of Hg in the canopy and forest floor.

Most of the Hg input to the forest floor is inherently associated with organic matter by virtue of its incorporation in litterfall. Mercury reaching the forest floor by other means -- direct precipitation or washoff of particulate dry deposition -- also likely associates with organic matter [Aastrup *et al.*, 1991; Mierle and Ingram, 1991]. Mercury concentrations in forest floor soil solution collected during storms at Nettle Brook were an order of magnitude greater than those in streamwater (Figure 6), suggesting that forest floor Hg may be flushed during storms. The positive correlation of Hg and DOC in soil water suggests that Hg is associated with dissolved organic acids. These mobile organic ions may help transport Hg to a stream, or downward in the profile where they adsorb to larger soil particles (causing the decrease in Hg concentrations in B-horizon soil water). Bishop *et al.* [1998] found that conifers took up small but variable amounts of Hg in soil water, depending on the tree species. Applying the results of Bishop *et al.* [1998] to soil water Hg concentrations at Nettle Brook, Rea [1998] estimated that between 3 and 14% of Hg in litterfall could be accounted for by uptake of soil water Hg.

What is the fate of the large pool of Hg "retained" in the catchment, represented by the large difference between the incoming flux of Hg in atmospheric deposition and the outgoing flux in streamflow (Figure 7)? The unaccounted Hg may either exit the catchment by volatilization to the atmosphere [Siegel and Siegel, 1988; Hanson *et al.*, 1995; Johnson and Lindberg, 1995], or it may remain in the catchment and accumulate in the soil. Volatilization in the terrestrial landscape occurs from foliar surfaces as well as from the forest floor, but its importance is poorly quantified.

Lindberg [1997] estimated that $657 \text{ mg ha}^{-1} \text{ yr}^{-1}$ Hg was volatilized from soil at a Tennessee site; Bishop *et al.* [1998] estimated $90 \text{ mg ha}^{-1} \text{ yr}^{-1}$ for a site in Sweden. Given the similarity in climate between Sweden and Vermont, the latter figure may more closely approximate the re-emission flux at Nettle Brook. If re-emission of Hg is of this magnitude, the input-output balance requires that a somewhat greater amount of Hg accumulate in catchment soils. Using some basic assumptions to convert the soil Hg concentrations to Hg pools (O-horizon: thickness = 8 cm; density = 1.1 g cm^{-3} ; porosity = 0.6; B-horizon: thickness = 20 cm; density = 2.5 g cm^{-3} ; porosity = 0.4), the existing Hg pool in the O-horizon can be accounted for by 150 years of deposition at the current rate; the combined Hg pool in the O- and B-horizons would require 600 years. It is not known how much of the soil Hg would be present naturally.

AQUATIC PROCESSES

On an annual basis, about 67% of Hg export is in the form of particulate Hg (primarily during high-flow events) and about 33% is as Hg_D. The tendency for event-related transport is reflected in the 3-month period of March-May, when about 84% of the annual flux of total Hg occurred with only 56% of the annual streamflow (Figure 7). The concentration of Hg_D remains fairly constant regardless of discharge [Scherbatskoy *et al.*, 1998], leading to a more "continuous" export of Hg_D in contrast to the episodic export of Hg_T.

As summarized in Scherbatskoy *et al.* [1998], Hg concentrations at Nettle Brook are typical of upland forested catchments for Hg_D and Hg_T, except at high flows. During events, Hg concentrations at Nettle Brook exceeding 20 ng L⁻¹ are among the highest reported in the literature. For example, among several catchments in Sweden, maximum Hg concentrations did not exceed 15 ng L⁻¹ [Johanssen *et al.*, 1991; Lee and Iverfeldt, 1991; Hultberg *et al.*, 1995] except for 21 ng L⁻¹ in runoff from a peat bog [Westling, 1991].

What controls Hg concentrations during high-flow events? Hg concentrations in Nettle Brook tend to increase with increasing stream discharge in a complex fashion, generally in conjunction with increased sediment transport at higher flows [Scherbatskoy *et al.*, 1998]. Total Hg concentrations attained very high values in the 1994 spring snowmelt (79.7 ng L⁻¹) and the 1996 January thaw (20.4 ng L⁻¹) [Scherbatskoy *et al.*, 1998]; these were not matched in subsequent sampling in 1996 and 1997, despite a focus on high-flow sampling in the latter year (Figure 3). In one of the few studies that conducted event sampling for Hg, Bishop *et al.* [1995] also found a positive correlation between Hg and flow during snowmelt in Sweden, although their streamwater Hg concentration peaked at only 6 ng L⁻¹, compared to 80 ng L⁻¹ at Nettle Brook. Bishop *et al.* [1995] found that 37% of total annual Hg flux occurred in a three week spring snowmelt period, compared to 50% in the single day of peak snowmelt in 1994 at Nettle Brook.

Scherbatskoy *et al.* [1998] found a good correlation between particulate Hg (Hg_T - Hg_D) and the organic fraction of suspended sediment. This relation is consistent with the known affinity of Hg(II) for organic matter in forest soils [Lindqvist, 1991; Mierle and Ingram, 1991; Schuster, 1991]. Total Hg was less well-correlated with stream DOC [Scherbatskoy *et al.*, 1998], but the most recent sampling has shown a strong relation between Hg_T and DOC (Figure 9). Driscoll *et al.* [1994] also found a positive correlation between Hg_T and DOC in Adirondack lakes. Likewise, in a small forested stream in Wisconsin, Krabbenhoft *et al.* [1995] found that Hg_T increased sharply with releases of DOC, while Me-Hg did not. Bishop *et al.* [1995] found that the increase in Hg concentration during the spring snowmelt was associated with total organic carbon.

A critical question is whether the occasional high episodic fluxes of Hg from upland catchments persist downstream to the larger rivers and to Lake Champlain. Synoptic sampling of some larger streams downstream of Nettle Brook [Scherbatskoy *et al.*, 1997] suggest that Hg dynamics are similar to those in the headwater catchment. As at Nettle Brook, Hg_D is consistently 1 to 3 ng L⁻¹ in the larger streams, but concentrations of Hg_T increase during large events, such as the 1994 snowmelt or the August 1995 flood (Figure 5). These episodic pulses of Hg in the larger rivers may reflect transport from steep upland headwater catchments such as Nettle Brook, or they may be caused by more local sources such as runoff from agricultural or disturbed lands. This important question is the subject of ongoing research.

The Hg output flux from Lake Champlain was estimated above as 15 mg ha⁻¹ yr⁻¹. This compares to 25-30 mg ha⁻¹ yr⁻¹ Hg entering from inlet streams and an equal amount of Hg from direct atmospheric deposition to the lake surface. Much of the excess Hg is probably incorporated in lake sediment (some passing first through the food chain), whereas some Hg is probably evaded from the lake surface.

CONCEPTUAL MODEL OF HG CYCLING IN THE BASIN

The small flux of Hg in streamflow relative to inputs in atmospheric deposition raises several questions about the fate of the Hg remaining in the catchment. How is Hg sequestered in the terrestrial landscape, and what internal processes control its release to surface waters? How much Hg is volatilized to the atmosphere, and how much of the remaining terrestrial Hg pool is cycled within the catchment? We have presented thus far a summary of the existing state of knowledge about Hg pools and fluxes in the Lake Champlain basin (Figure 8). Although many gaps and questions remain, the following is an attempt to synthesize our existing understanding into a conceptual model of Hg cycling in the basin.

Mercury enters the basin primarily from the atmosphere [NESCAUM *et al.*, 1998], and is therefore relatively uniformly distributed throughout the basin. Because the primary mechanism of dry deposition is by absorption through leaf stomata, total deposition is influenced by land cover type. Stomatal density in agricultural cropland at maturity may be comparable to that of a forest, but vegetation is removed by harvesting. Accordingly, deposition may be lower in agricultural and developed areas. In any case, of the Hg incident to the landscape, whether absorbed by foliage or passing to land surface, a sizeable fraction is re-volatilized to the atmosphere. The remaining Hg becomes bound by soil organic matter, the majority (in the forested landscape) as litterfall.

The pool of Hg in the forest floor establishes equilibrium with soil solution. A small amount of the dissolved Hg in soil solution is translocated to foliage by root uptake and returns to the foliage/litterfall/forest floor cycle [Bishop *et al.*, 1998; Rea, 1998]. Some of the Hg in soil solution moves to the stream in association with DOC. Another portion of the Hg moves with water seeping deeper in the soil where it establishes equilibrium at a lower Hg concentration. Mercury reaching the groundwater supplies the low base flow Hg concentrations in streamwater. The higher stormflow Hg_T concentrations result from erosion of streambanks or riparian soils and/or mobilization of organic-rich stream sediments. Because of the linkage of Hg transport and suspended sediment concentrations, erosion-prone farmlands and developed lands may be more important Hg sources than the forest, but this possibility cannot be assessed from existing data.

The low but constant dissolved Hg concentrations in streamwater suggest a constant transfer of Hg from the basin to Lake Champlain. The higher episodic transport of particulate Hg is reflected in elevated Hg concentrations downstream as well, and represents pulse Hg inputs. Reduced gradients on approach to the lake result in sediment deposition and Hg accumulation in stream and lake sediments, but these deposits are likely periodically remobilized during subsequent storms. Available data preclude determining whether farmlands and developed lands contribute to the episodic Hg pulses in downstream locations. Mercury reaching the lake, whether by stream inputs or direct deposition to the lake surface, is divided among uptake in the food chain, deposition in sediment, evasion from the lake surface, and export from the lake outlet.

Nearly all of the terrestrial Hg research in the Lake Champlain basin has been in the forested environment. While forests represent the major land cover in the basin, the linkage between sediment and Hg suggests that agricultural and urban land uses may export considerable Hg. An agricultural landscape in Minnesota [Balogh *et al.*, 1997] and an urban landscape near Washington D. C. [Mason and Sullivan, 1998] export more Hg than a typical undisturbed forest. Our current research on Hg cycling in the Lake Champlain basin is addressing the role of the agricultural landscape.

MERCURY AND HUMAN HEALTH

Mercury bioaccumulates in fish to levels that are potentially dangerous to humans, even though the concentrations in water and sediments are very low. No specific studies have been done in the basin on Hg in the food web, but our limited data suggest that Me-Hg increases up the food chain. Total Hg concentrations increased from lake sediment (a mixture of organic detritus with inorganic matter) (200 ng g^{-1}) [MacIntosh, 1994]; to small plankton (410 ng g^{-1} ; 5 ng g^{-1} Me-Hg); to large plankton (760 ng g^{-1} ; 21 ng g^{-1}

Me-Hg); to fish (100-2000 ng g⁻¹ wet weight). The Hg concentrations in fish would be several times higher if expressed on a dry weight basis similar to the plankton. Walleye and lake trout may have some of the highest Hg contents because they subsist almost exclusively on other fish.

Methylmercury, the form of Hg toxic to humans, is generally present in waters in much lower concentrations than Hg_T, but it comprises greater than 95% of the Hg in fish [Porcella, 1994]. Fish do not methylate inorganic Hg within their tissues, but rather obtain Me-Hg from their diet, and to a lesser extent, through their gills [Weiner and Spry, 1996]. Generally less than 1% of Hg in atmospheric deposition is as Me-Hg [Porcella, 1994]. Methylmercury is formed subsequent to Hg deposition under reducing conditions such as in wetlands [Krabbenhoft *et al.*, 1995; Branfireun *et al.*, 1996] and in stream and lake sediments, soils, and lake water [Verta *et al.*, 1994]. Some studies suggest that wetlands are primarily responsible for Me-Hg mobilization [Driscoll *et al.*, 1994; Hurley *et al.*, 1995; Branfireun *et al.*, 1996]. In the Experimental Lakes Area of Ontario, Me-Hg ranged between 0.46% and 31% of Hg_T, but peaked as high as 92% after a flood in an experimental wetland [Kelly *et al.*, 1995]. Mercury dynamics in wetlands have not been investigated in the Lake Champlain basin.

Methylmercury concentrations were determined on a small set of samples from Lake Champlain waters [M. Watzin, University of Vermont, unpublished data]. Methylmercury concentrations were extremely low, on the order of 0.03 ng L⁻¹, while corresponding Hg_T concentrations were near 1.2 ng L⁻¹. Methylmercury concentration was 0.23 ng L⁻¹ on the Browns River. When one considers that nearly all the Hg in fish is in the Me-Hg form, and that the starting Me-Hg concentration in waters is so very low, this is strong testimony to the bioconcentration of Me-Hg.

CONCLUSIONS

The Lake Champlain basin receives about 450 mg ha⁻¹ yr⁻¹ Hg in atmospheric deposition. About 30% is wet deposition and 70% is dry deposition, mostly by absorption through leaf stomata. Some of the incident Hg is re-emitted to the atmosphere; most of the remainder is sequestered in the forest floor by organic matter, including a large portion in litterfall. Only a minor amount of this forest floor Hg pool reaches a surface stream; in 2 years of study, only 5 to 8% of the incident Hg was exported in streamflow. Stream Hg export occurred as a small but constant dissolved Hg flux (about one-third) and an episodic organic-particulate Hg flux (about two-thirds). High Hg concentrations in O-horizon soil water suggest that the upper soil zone is a primary pathway for Hg from the terrestrial ecosystem to the stream.

Larger streams exhibit similar Hg dynamics to the headwater Nettle Brook. However, we do not know whether Hg transported in mountain streams consistently reaches the lowlands, or whether the more proximal agricultural and developed landscapes contribute to the observed episodic Hg pulses. Dissolved Hg concentrations in Lake Champlain itself are similar to observed concentrations of dissolved Hg in streamwater. Particulate Hg is probably incorporated in lake sediments. Some Hg enters the food chain, and bioaccumulation has elevated Hg concentrations in some fish species to levels that are hazardous for human consumption. Mercury uptake and accumulation in fish is nearly exclusively as Me-Hg; human health risks should be assessed in light of methylation potential.

Acknowledgments. Support was provided from EPA and NOAA through the Cooperative Institute of Limnology and Ecosystems Research agreement no. NA37RJ0204. We wish to acknowledge the University of Vermont Proctor Maple Research Center and the assistance of Joanne Cummings and Jon Denner. This research was undertaken in cooperation with the Vermont Forest Ecosystem Monitoring Program. The manuscript benefitted greatly from reviews by two anonymous reviewers.

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, and Soil Pollution* 56: 155-167.
- Back, R. C., V. Visman, and C. J. Watras. 1995. Microhomogenization of individual zooplankton species improves mercury and methylmercury determinations. *Canadian Journal of Fisheries and Aquatic Sciences* 52: 2470-2475.
- Balogh, S. E., M. D. Meyer, and D. K. Johnson. 1997. Mercury and suspended sediment loadings in the lower Minnesota River. *Environmental Science and Technology* 31: 198-202.
- Bishop, K., Y. -H. Lee, J. Munthe, and E. Dambrine. 1998. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. *Biogeochemistry* 40: 101-113.
- Bishop, K., Y. -H. Lee, C. Pettersson and B. Allard. 1995. Methylmercury output from the Svartberget catchment in northern Sweden during spring flood. *Water, Air, and Soil Pollution* 80: 445-454.
- Branfireun, B. A., A. Heyes, and N. T. Roulet. 1996. The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. *Water Resources Research* 32: 1785-1794.
- Burke, J., M. Hoyer, G. J. Keeler, and T. Scherbatskoy. 1995. Wet deposition of mercury and ambient mercury concentrations at a site in the Lake Champlain Basin. *Water, Air, and Soil Pollution* 80: 353-362.
- Cleckner, L. B., E. S. Esseks, P. G. Meier, and G. J. Keeler. 1995. Mercury concentrations in two "Great Waters." *Water, Air, and Soil Pollution* 80: 581-584.
- Colman, J. A. and S. F. Clark. 1994. *Geochemical Data on Concentrations of Inorganic Constituents and Polychlorinated Biphenyl Congeners in Streambed Sediments in Tributaries to Lake Champlain in New York, Vermont, and Québec, 1992*. U.S. Geological Survey Open-File Report 94-472, 65 pp.
- Driscoll, C. T., C. Yan, C. L. Schofield, R. Munson, and J. Holsapple. 1994. The mercury cycle and fish in Adirondack lakes. *Environmental Science and Technology* 28:136A-143A.
- Engstrom, D. R. and E. B. Swain. 1997. Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environmental Science and Technology* 31: 960-967.
- Fitzgerald, W. F. 1993. Mercury as a global pollutant. *The World & I*. October: 192-198.
- Fitzgerald, W. F., D. R. Engstrom, R. P. Mason, and E. A. Nater. 1998. The case for atmospheric mercury contamination in remote areas. *Environmental Science and Technology* 32: 1-7.
- Haines, T., B. Mower, and R. Perry. 1995. Regional patterns of mercury content in snowpack, sphagnum, and fish in northeastern North America. Poster presented at Society of Environmental Chemistry and Toxicology Second World Congress, Vancouver, BC, Canada. Nov. 5-9, 1995.
- 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, and Soil Pollution* 80: 373-382.
- Hem, J. D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*. U.S. Geological Survey Water Supply Paper 2254, 263 pp.
- Hoyer, H., J. Burke, and G. J. Keeler. 1995. Atmospheric sources, transport and deposition of mercury in Michigan: two years of event precipitation. *Water, Air, and Soil Pollution* 80: 199-208.
- Hultberg, H., J. Munthe, and A. Iverfeldt. 1995. Cycling of methyl mercury and mercury -- responses in the forest roof catchment to three years of decreased atmospheric deposition. *Water, Air, and Soil Pollution* 80: 415-424.
- 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. *Environmental Science and Technology* 29: 1867-1875.
- Johansson, K., M. Aastrup, A. Andersson, L. Bringmark, and A. Iverfeldt. 1991. Mercury in Swedish soils and waters - assessment of critical load. *Water, Air, and Soil Pollution* 56: 267-281.
- Johnson, D.W. and S. E. Lindberg, S.E. 1995. The biogeochemical cycling of Hg in forests: alternative methods for quantifying total deposition and soil emission. *Water, Air, and Soil Pollution* 80: 1069-1077.
- Keeler, G. J., G. Glinsorn, and N. Pirrone. 1995. Particulate mercury in the atmosphere: its significance, transport, transformation, and sources. *Water, Air, and Soil Pollution* 80: 159-168.
- Kelly, C. A., J. W. M. Rudd, V. L. St. Louis, and A. Heyes. 1995. Is total mercury concentration a good predictor of methylmercury concentration in aquatic systems? *Water, Air, and Soil Pollution* 80: 715-724.
- Krabbenhof, 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, and Soil Pollution* 80: 425-433.

- Landis, M. S. and G. J. Keeler. 1997. Critical evaluation of a modified automatic wet-only precipitation collector for Hg and trace element determinations. *Environmental Science and Technology* 31: 2610-2615.
- Lee, Y. -H. and A. Iverfeldt. 1991. Measurement of methylmercury and mercury in run-off, lake and rain waters. *Water, Air, and Soil Pollution* 56: 309-321.
- Lindberg, S. E. 1993. *Journal of Geophysical Research* 97: 14677.
- Lindberg, S. E. 1997. Forests and the global biogeochemical cycle of mercury: the importance of understanding air/vegetation exchange processes. In: Baeyens, W. and O. Vasiliev, eds. *Global and Regional and Mercury Cycles: sources, fluxes, and mass balances*. NATO Advanced Science Institute. Boston, Massachusetts: Kluwer Academic.
- Lindberg, S. E., T. P. Meyers, G. E. Taylor, R. R. Turner, and W. H. Schroeder. 1992. Atmosphere-surface exchange of mercury in a forest: results of modeling and gradient approaches. *Journal of Geophysical Research* 97: D-2: 2519-2528.
- Lindqvist, O. 1991. Mercury in the Swedish environment. Chapter 8: Mercury in terrestrial systems. *Water, Air, and Soil Pollution* 55: 73-100.
- MacIntosh, A. (ed.). 1994. *Lake Champlain Sediment Toxics Assessment Program: an assessment of sediment associated contaminants in Lake Champlain, Phase I*. Lake Champlain Technical Report No. 5, Lake Champlain Basin Program, Grand Isle, Vermont.
- Mason, R. P. and K. A. Sullivan. 1997. Mercury in Lake Michigan. *Environmental Science and Technology* 31: 942-947.
- Mason, R. P. and K. A. Sullivan. 1998. Mercury and methylmercury transport through an urban watershed. *Water Resources Research* 32(2): 321-330.
- Mierle, G. and R. Ingram. 1991. The role of humic substances in the mobilization of mercury from watersheds. *Water, Air, and Soil Pollution* 56: 349-357.
- Miskimmin, B. M., J. W. M. Rudd, and C. A. Kelly. 1992. Influence of dissolved organic carbon, pH, and microbial respiration rates on mercury methylation and demethylation in lake water. *Canadian Journal of Fisheries and Aquatic Sciences*. 49: 17-22.
- NESCAUM (Northeast States for Coordinated Air Use Management), NEWMOA (Northeast Waste Management Officials Association), NEIWPCC (New England Interstate Water Pollution Control Commission), and EMAN (Canadian Ecological Monitoring and Assessment Network). 1998. *Northeast States and Eastern Canadian Provinces Mercury Study: a framework for action*. February, 1998.
- Nriagu, J. O. and J. M. Pacyna. 1988. Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. *Nature* 333: 134-139.
- Olmez, I., M. R. Ames, and G. Gullu. 1998. Canadian and U.S. sources impacting the mercury levels in fine atmospheric particulate material across New York State. *Environmental Science and Technology* 32: 3048-3054.
- Porcella, D.B. 1994. Mercury in the environment: biogeochemistry. In: C. J. Watras and J. W. Huckabee (eds.), *Mercury Pollution: Integration and Synthesis*. Boca Raton: Lewis Publishers. p. 3-19.
- Rea, A. W. 1998. Accumulation of atmospheric mercury in foliage in the Lake Champlain and Lake Huron watershed. Ph.D. dissertation, University of Michigan, University Microfilms, Inc.
- Rea, A. W., G. J. Keeler and T. Scherbatskoy. 1996. The deposition of mercury in throughfall and litterfall in the Lake Champlain watershed: a short-term study. *Atmospheric Environment* 30: 3257-3263.
- River Watch Network. 1998. *River Peoples of Color Project, Final Report*. U. S. EPA Environmental Justice Small Grants Program, 7 pp.
- Scherbatskoy, T., J. M. Burke, A. W. Rea, and G. J. Keeler. 1997. Atmospheric mercury deposition and cycling in the Lake Champlain Basin of Vermont. In: J.E. Baker (ed.), *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*. Society of Environmental Toxicology and Chemistry Special Publication Series. Pensacola, FL: SETAC Press, Pensacola, FL.
- Scherbatskoy, T., J. B. Shanley, and G. J. Keeler. 1998. Factors controlling mercury transport in an upland forested catchment. *Water, Air, and Soil Pollution* 105: 427-438.
- Schuster, E. 1991. The behavior of mercury in the soil with special emphasis on complexation and adsorption processes -- a review of the literature. *Water, Air, and Soil Pollution* 56: 667-680.
- Siegel, S.M. and B. Z. Siegel. 1988. Temperature determinants in plant-soil-air mercury relationships. *Water, Air, and Soil Pollution* 40: 443-448.
- Slemr, F. and E. Langer. 1992. Increase in global concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature* 355:434-437.
- State of Vermont. 1990. *Fish Contaminant Monitoring Program Report*, 4 pp.
- State of Vermont. 1997. *A Compendium of Fish Tissue Contaminant Data from Vermont and Adjoining Waters 1970-1990*, 56 pp.

- 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* 257: 784-787.
- United States Environmental Protection Agency. 1997. *Mercury Study Report to Congress*. Office of Air Quality Planning and Standards and Office of Research and Development. Washington, D. C. EPA-452/R-97-003. December 1997.
- Vasu, A. B. and M. L. McCullough. 1994. *First Report to Congress on Deposition of Air Pollutants to the Great Waters*. U.S. EPA Office of Air Quality and Planning Standards, Research Triangle Park, North Carolina. EPA-453/R-93-055.
- Vermont DEC. 1996. *June 4-11, 1996, Emission Test Report Review of SMS Incinerator*. August 28, 1996. Air Pollution Control Division.
- Verta, M., T. Matilainen, P. Porvari, M. Niemi, A. Uusi-Rauva, and N. S. Bloom. 1994. Methylmercury sources in boreal lake ecosystems. In: C.J. Watras and J.W. Huckabee (eds.), *Mercury Pollution: Integration and Synthesis*. Boca Raton: Lewis Publishers, p. 119-136.
- Watzin, M. C. 1992. A research and monitoring agenda for Lake Champlain: proceedings of a workshop, December 17-19, Burlington, VT. *Lake Champlain Basin Program Technical Report No. 1*. U.S. EPA, Boston, Massachusetts.
- Weiner, J. G. and D. J. Spry. 1996. Toxicological significance of mercury in freshwater fish. In: Beyer, W. N., G. H. Heinz, and A. W. Redmon-Norwood (eds.), *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*. New York: Lewis Publishers, Inc.
- Westling, O. 1991. Mercury in runoff from drained and undrained peatlands in Sweden. *Water, Air, and Soil Pollution* 56: 419-426.
- Wilmot, S. H. and T. Scherbatskoy. 1994. *Vermont Monitoring Cooperative Annual Report for 1993*. VMC Annual Report Number 3. Vermont Department of Forests, Parks, and Recreation, Waterbury, Vermont.

Figure 1. Map showing sampling locations. Left panel shows the Lake Champlain drainage basin with sites along the Lamoille River. Right panel shows a close-up of sites in Underhill Center, Vermont. Sampling sites are as follows: (1) Lamoille River at West Milton, (2) Browns River, (3) Lamoille River at Jeffersonville, (4) Harvey Brook, (5) Proctor Maple Research Center, (6) Stream 10, and (7) Nettle Brook.

Figure 2. Boxplot indicating total Hg concentrations at all surface water sites in Lake Champlain basin with available data [Cleckner *et al.*, 1995; Scherbatskoy *et al.*, 1997; 1998]. Site locations are described in text and/or shown in Figure 1. For each site, stippled area spans concentration range from 25th to 75th percentile, with horizontal line denoting median; horizontal tick above and below stippled areas represents 10th and 90th percentile; points are individual values beyond 90th percentile.

Figure 3. Discharge (mm hr^{-1}) and stream water total Hg concentration (ng L^{-1}) at the Nettle Brook weir from March 1994 through September 1997. Water was sampled for Hg analysis on a daily basis during spring snowmelt and periodically during the remainder of the year.

Figure 4. Concentration - discharge relation for total Hg at Nettle Brook, differentiating samples from 2 different time periods. Open circles: Scherbatskoy *et al.* [1998]; Closed squares: previously unpublished data.

Figure 5. Total Hg concentrations at the Lamoille River and Browns River sites for base flow and selected events, plotted as a function of normalized discharge at a nearby USGS gaging station.

Figure 6. Soil water (from Oa and B soil horizons) and stream concentrations of total Hg and dissolved organic carbon (DOC), and Hg concentrations in soils at three locations in Underhill Center, Vermont. Stream (D) refers to dissolved Hg concentrations in stream water; stream (T) refers to total Hg concentrations in stream water.

Figure 7. Seasonal input (wet and dry deposition) and stream export (dissolved and particulate) of total Hg in Nettle Brook catchment from December 1993 through February 1996, expressed as mg ha^{-1} . Modified from Scherbatskoy *et al.* [1998].

Figure 8. Schematic depicting fluxes of Hg ($\text{mg ha}^{-1} \text{yr}^{-1}$) in the Lake Champlain basin. Superscript numbers indicate the derivation of fluxes as follows: 1. NESCAUM *et al.*, 1998 (bars are proportional based on percentages); 2. Scherbatskoy *et al.*, 1998; 3. Scherbatskoy *et al.*, 1998; 4. Bishop *et al.*, 1998 (site in Sweden - assumed Vermont is similar); 5. Rea [1998]; 6. Rea *et al.*, 1996; extrapolated to 6 month growing season from 2 month study; 7. Rea [1998]; 8, 9, 10. Estimated from consideration of soil pools [this paper], and stream Hg dynamics [Scherbatskoy *et al.*, 1998], constrained to match stream flux; 11. Scherbatskoy *et al.*, 1998; 12. Total deposition [Scherbatskoy *et al.*, 1998] prorated to lake area; 13. Estimated from Hg concentration in lake [Cleckner *et al.*, 1995] and mean annual lake discharge [Shanley and Denner, this volume].

Figure 9. Total Hg concentration as a function of DOC at Nettle Brook during 1997.

TABLE 1. Inputs and outputs of water and mercury at Nettle Brook catchment for two study years (From Scherbatskoy *et al.* [1998])

Date	Water		Mercury			Retention			
	Precip. (mm)	Stream flow (mm)	<i>Input (mg Hg ha⁻¹)</i>				<i>Output (mg Hg ha⁻¹)</i>		
			Wet	Dry	Total	Particulate	Dissolved	Total	
3/94 - 2/95	1139	587	74.5	350	425	23.6	8.4	31.9	92%
3/95 - 2/96	1109	568	92.7	370	463	13.4	8.2	21.7	95%

TABLE 2. Sediment Hg concentrations ($\mu\text{g g}^{-1}$) in Lake Champlain and inlet streams

	n	median	mean	std. dev.
Streams [Colman & Clark, 1994]	76	0.18	0.29	0.43
Lake [MacIntosh, 1994]	30	0.20	0.20	0.15

Figure 1.

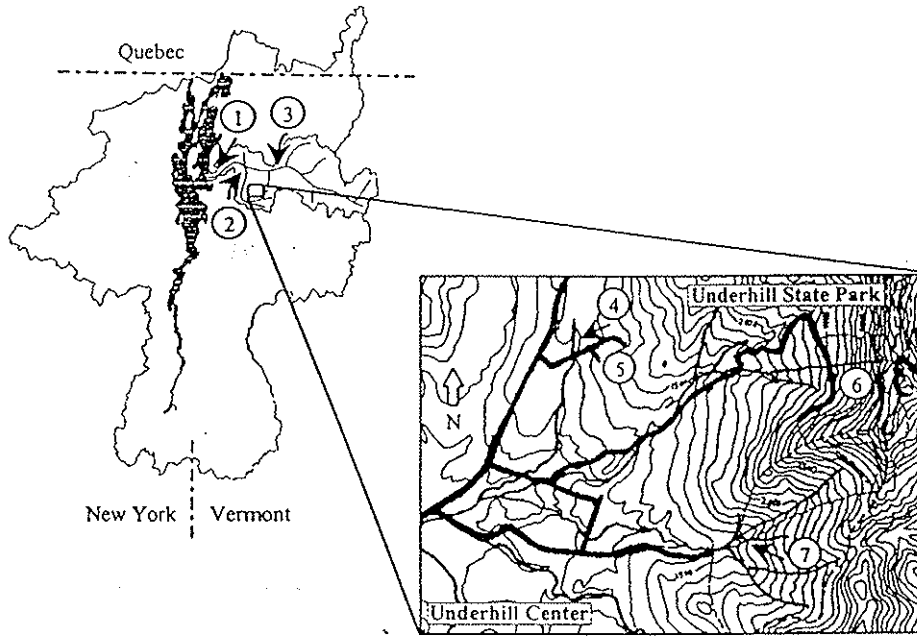


Figure 2

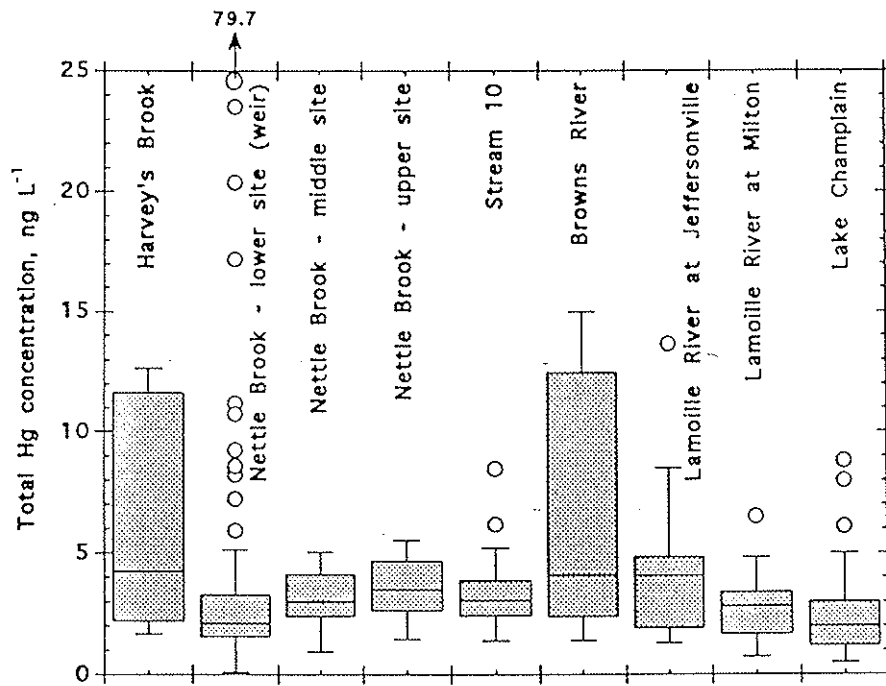


Figure 5

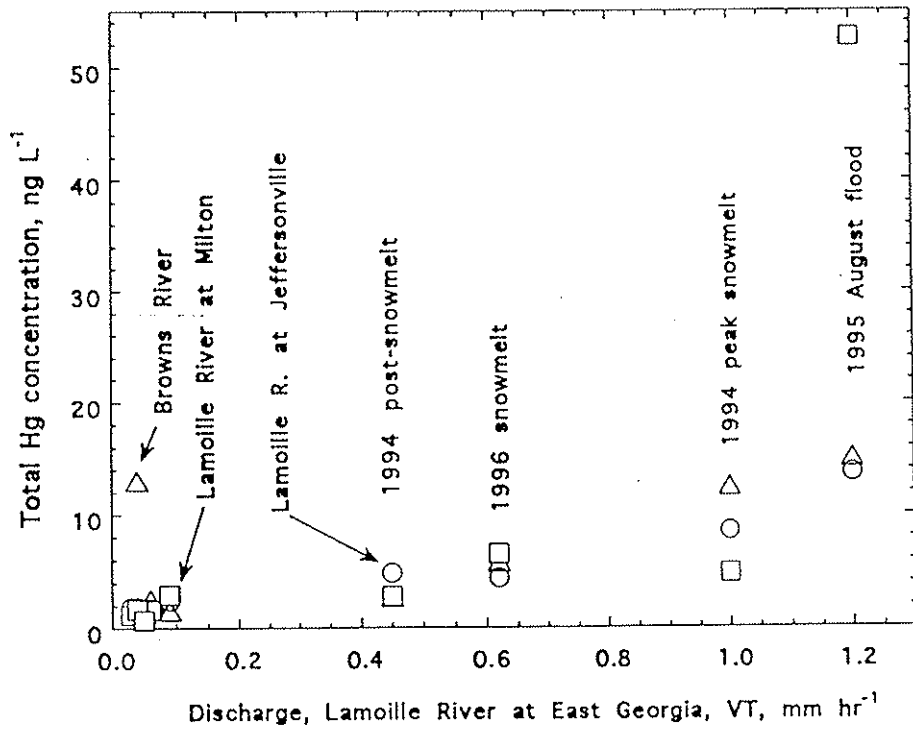


Figure 6

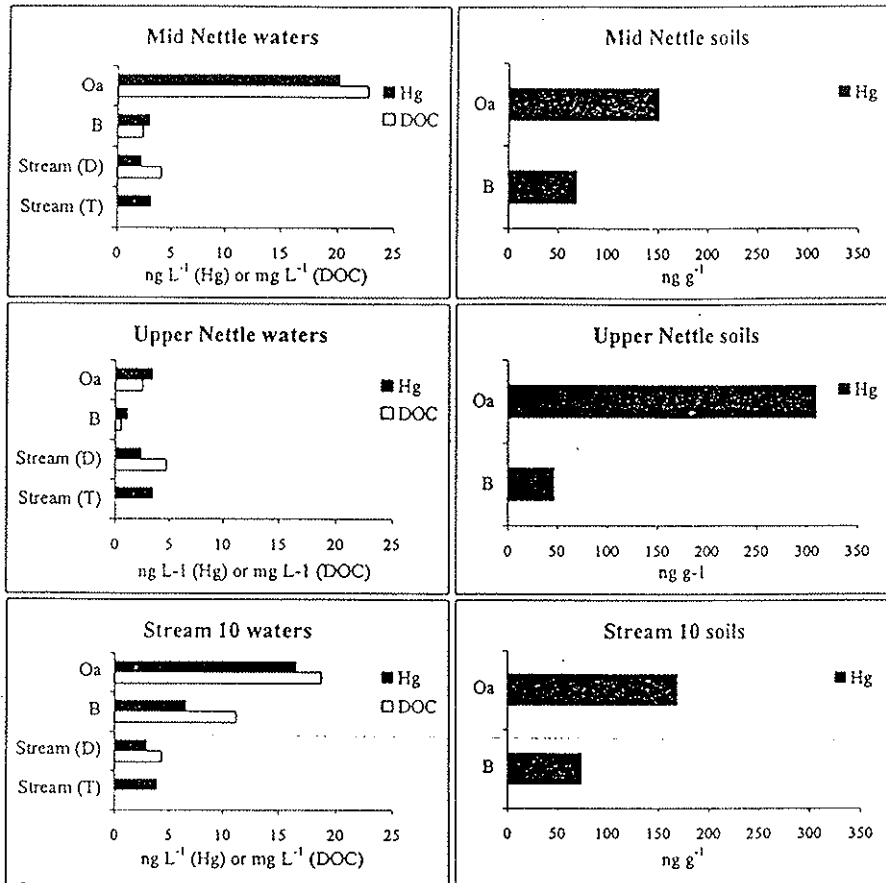


Figure 7

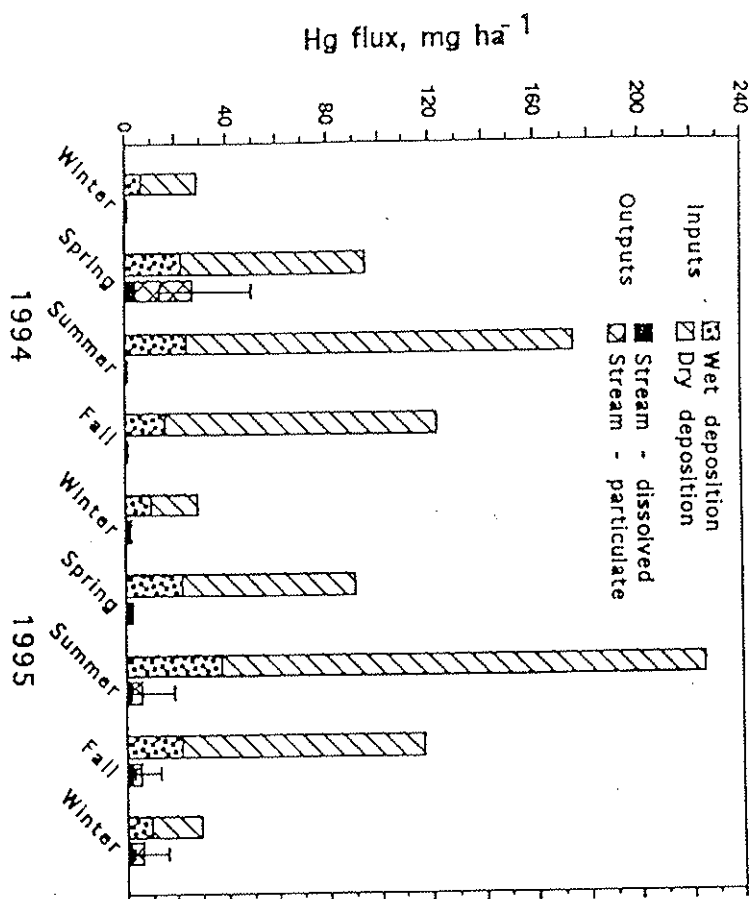


Figure 8

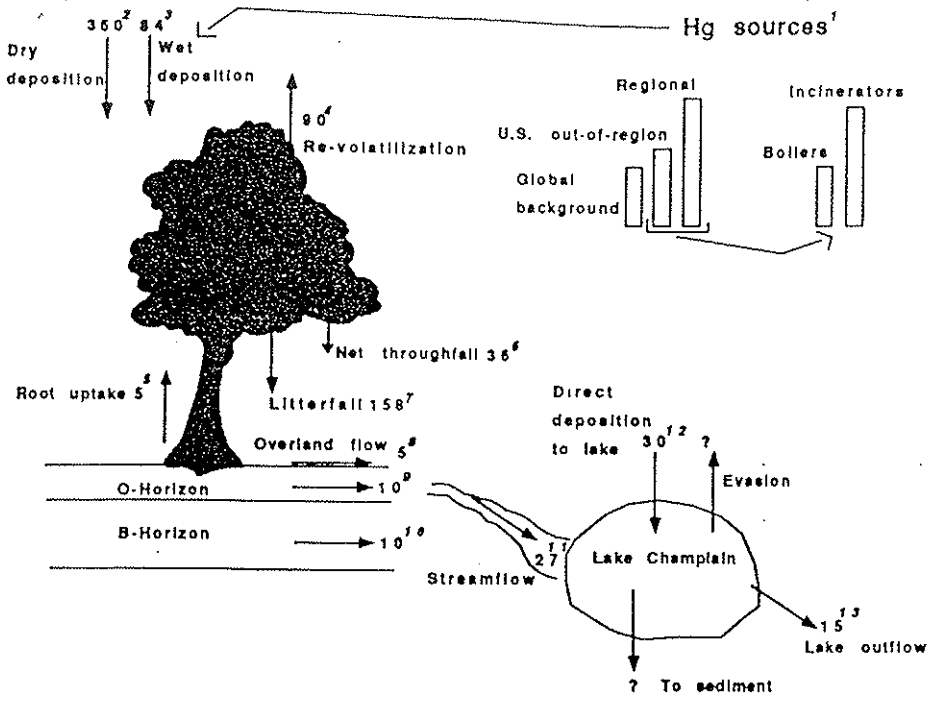


Figure 9

