

# Deposition and within-forest processing of atmospheric mercury - 1994 -

Tim Scherbatskoy  
University of Vermont School of Natural Resources

## Cooperators:

University of Vermont: Joanne Cummings, Carl Waite, Rinda Gordon  
Proctor Maple Research Center: Melvin Tyree, Sumner Williams  
University of Michigan: Jerry Keeler, Anne Rea  
NOAA Air Resources Laboratory: Richard Artz  
VT ANR DEC Air Pollution Control Program: Rich Poirot

## Abstract:

Deposition and ecosystem processing of atmospheric mercury (Hg) in the Lake Champlain basin has been studied in cooperation with the University of Michigan Air Quality Laboratory since December, 1992 at the VMC Air Quality Monitoring site in Underhill Center, VT (400 m elevation). Daily wet-only precipitation, weekly 24 hr vapor and particulate samples, snowmelt and stream water have been analyzed for total Hg by cold vapor atomic fluorescence spectrometry (CVAFS). Between December 1992 and December 1994, total mercury in precipitation ranged from 1.5 to 44 ng/L; the highest concentrations generally occurred during the summer months. Vapor phase Hg ranged from 1.2 to 4.2 ng/m<sup>3</sup>, without much seasonal variation. Particulate phase Hg ranged from 1 to 43 pg/m<sup>3</sup>, with the highest concentrations occurring in the winter months. Wet deposition of total Hg in precipitation totaled 9.27  $\mu\text{g}/\text{m}^2$  for 1993 and 7.66  $\mu\text{g}/\text{m}^2$  for 1994. Combined wet and dry deposition of Hg, using estimated vapor phase dry deposition, was 15.0  $\mu\text{g}/\text{m}^2$  for 1993 and 12.5  $\mu\text{g}/\text{m}^2$  for 1994, with the greatest deposition rates in the summer months. In addition, total Hg concentrations in stream-water were monitored in Nettle Brook, a small stream draining an 11 ha mixed hardwood watershed in the Stevensville Brook area. Hg concentrations were 1 to 3 ng/L during base flow conditions, and reached 79 ng/L at peak flow during spring snowmelt. Synoptic sampling of rivers in the same drainage basin also showed significant increases in total Hg during snowmelt periods. Measurements of Hg chemistry of snow-pack and snow-melt were also conducted in 1994, and are summarized here. Finally, an intensive study of Hg in forest canopy throughfall was conducted during the summer of 1994, showing that Hg is significantly enriched in throughfall and that autumn litterfall provides a very large flux of Hg to the forest floor.

## INTRODUCTION

There is widespread concern that atmospheric sources of mercury (Hg) may be responsible for increasing Hg burdens in Lake Champlain (McIntosh 1994, Vasu and McCullough 1994). This has been shown to be the case for many remote lakes in the Great Lakes region (Fitzgerald *et al.* 1991), but there are no comparable data for the Lake Champlain basin. Little information exists on levels or behavior of Hg in forested ecosystems, but these may provide important pathways for the transport and transformation of Hg from the atmosphere to aquatic systems. The Lake Champlain basin is characterized by a large (18:1) ratio of watershed to lake surface area, so capture and processing of atmospheric pollutants by forest systems is particularly important to understand in this region (Table 1). Approximately 89% of the basin is in forest and agriculture categories, with the lake itself representing only 5% of the total basin area. This is in sharp contrast to the Great Lakes, which represent a large proportion of their watersheds.

The research program discussed here was established to address concerns about Hg and other toxic metals in the aquatic, terrestrial and atmospheric systems of the Lake Champlain basin. The broad goals of this program include: (1) characterizing Hg concentration and deposition in precipitation, particulate and vapor phases, (2) studying Hg transport and processing within forested watersheds (including snowmelt, stream chemistry and transport, and forest throughfall), and (3) supporting larger Lake Champlain issues (meso-scale modeling of pollutant deposition, trace metal toxicology, and patterns of accumulation of toxics in biota and sediments). From 1992 to 1994, work concentrated on monitoring Hg concentrations in precipitation, vapor and particulate phases, and on obtaining baseline data for Hg and trace metals in stream water and snow-melt. Subsequent work is aimed at developing a better understanding of Hg cycling, mass balance, transport mechanisms and trophic relationships in the ecosystems of the Lake Champlain basin.

## RESULTS

Two publications resulted from these studies in 1994. One deals with atmospheric Hg deposition and watershed transport processes (Scherbatskoy *et al.* 1995), and the other focuses on forest canopy throughfall and litterfall (Rea *et al.* 1995). Detailed explanations of objectives, methods and results are presented in these papers, and will not be repeated here. Instead, what follows is a brief synopsis and several tables and figures to briefly summarize key findings from this work through 1994.

### *Atmospheric Deposition*

Monthly average concentrations of total Hg in precipitation, vapor and particulate phases are summarized for 1993 and 1994 in Figure 1. Seasonal patterns are summarized in Tables 2 and 3. These data are comparable in magnitude and trend to values for rural northern Michigan (Burke *et al.* 1995, Hoyer *et al.* 1995, Keeler *et al.* 1995). Monthly wet and dry Hg deposition are shown for 1993 and part of 1994 in Figure 2; dry deposition was estimated from vapor phase Hg concentration as described in Scherbatskoy *et al.* (1995). The total Hg deposition for 1993 was calculated to be  $14.97 \mu\text{g}/\text{m}^2$ , consisting of  $9.27 \mu\text{g}/\text{m}^2$  wet and  $5.70 \mu\text{g}/\text{m}^2$  estimated dry deposition.

### *Surface Water Chemistry*

Since October 1993, stream major ion chemistry, flow and environmental parameters have been

monitored at Nettle Brook, draining an 11 ha catchment located within a mixed hardwood forest where detailed characterizations of the stream and forested watershed are being conducted. Mercury monitoring in this stream began in March 1994. Total Hg concentrations in streamwater during early spring 1994 are shown for this site in Figure 3. Maximum Hg concentration of 79 ng/L was measured during peak streamflow (76 L/s on 16 April). Hg concentration in the filtered water fraction (0.2  $\mu\text{m}$ ) were generally in the range of 2 to 3 ng/L even when flow and total Hg concentrations increased sharply. During the year, Hg export from the Nettle Brook watershed totaled 31 mg/ha (3.1  $\mu\text{g}/\text{m}^2$ ), approximately one-fifth of the total wet plus estimated dry deposition for this period (Figure 4). This suggests that a large portion of atmospherically deposited Hg may be retained in the watershed. Synoptic stream samples were also collected in 1994 on three dates at four sites in the Lamoille River drainage basin (Figure 5); these data are summarized in Figure 6 and show that the higher Hg concentrations associated with early spring snowmelt also occur in the larger rivers.

### *Snow chemistry*

The Hg chemistry of the accumulated snow-pack for winter 1994 is summarized in Table 4. Snow-melt, collected daily in early spring 1994 from a large Teflon-coated snow lysimeter, had a range of Hg concentration from 2 to 9.2 ng/L.

### *Throughfall*

Throughfall, green foliage, litterfall, precipitation and ambient air were analyzed for total Hg in a mixed hardwood stand at the forest canopy research tower at the Proctor Maple Research Center in Underhill Center during a six week period in August and September, 1994. During this period, the volume-weighted mean Hg concentration in throughfall ( $12 \pm 8.5$  ng/L) was greater than in precipitation ( $6.5 \pm 2.8$  ng/L); these data are summarized in Figure 7. Hg deposition in throughfall and precipitation during this period were 1.2  $\mu\text{g}/\text{m}^2$  and 1.9  $\mu\text{g}/\text{m}^2$ , respectively. Throughfall, therefore, represents a significant addition to total Hg deposition in forested areas. The mean concentration of Hg in litterfall ( $53.2 \pm 11.4$  ng/g) was greater than in green foliage ( $34.2 \pm 7.2$  ng/g), and annual Hg deposition in litter was estimated to be 13  $\mu\text{g}/\text{m}^2$  (Rea *et al.* 1995).

## REGIONAL CONTEXT

These studies were designed to provide basic monitoring data for atmospheric Hg deposition and to build toward understanding the processes controlling Hg deposition, transport, transformation and accumulation in the watersheds and streams of the Lake Champlain basin. The Hg monitoring site in Underhill Center is the eastern-most site in a 10-site Hg monitoring network operated by the University of Michigan Air Quality Laboratory, and is considered representative of the forested watersheds of the Lake Champlain basin. There is at present no other comparable monitoring program in New England that provides continuous monitoring of Hg in all three phases: precipitation, vapor and particulate. Future work will continue atmospheric and stream Hg monitoring, and will intensify efforts to identify mechanisms governing Hg transport and mass balance in forested watersheds, and basic trophic relationships in surface waters. These are the necessary components of an ecologically integrated analysis of Hg behavior in a complex ecosystem such as the Lake Champlain basin, and it is this kind of approach that will be required as we develop ecosystem management strategies to address the problems of persistent pollutants in the environment.

## ACKNOWLEDGEMENTS

Primary financial support for this work was from the NOAA Air Resources Lab (contract # USDC-40EANR-3000923 and others) under the Lake Champlain Special Designation Act of 1990, with additional support from the US EPA OAQPS Great Waters Program and the Vermont Air Pollution Control Division. We also wish to acknowledge the assistance and support of the University of Vermont Proctor Maple Research Center, where much of this work was conducted, and the very able assistance of Joanne Cummings and Carl Waite. This study was undertaken in cooperation with the Vermont Monitoring Cooperative.

## REFERENCES

- Budd, L. and D. Meals. 1994. Lake Champlain nonpoint source pollution assessment. Lake Champlain Basin Program. Grand Isle, Vermont.
- Burke, J., M. Hoyer, G. Keeler and T. Scherbatskoy. 1995. Wet deposition of mercury and ambient mercury concentrations at a site in the Lake Champlain Basin. *Water Air Soil Pollut.* 80:353-362.
- Fitzgerald, W.F., R.P. Mason and G.M. Vandal. 1991. Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. *Water Air Soil Pollut.* 56:745-767.
- Hoyer, M, J. Burke and J. Keeler. 1995. Atmospheric sources, transport and deposition of mercury in Michigan: two years of event precipitation. *Water Air Soil Pollut.* 80:199-208.
- McIntosh, A. (ed.). 1994. Lake Champlain sediment toxics assessment program: an assessment of sediment associated contaminants in Lake Champlain, Phase I. Lake Champlain Basin Program Technical Report No. 5. Lake Champlain Basin Program, Grand Isle, Vermont.
- Rea, A.W., G.J. Keeler and T. Scherbatskoy. 1995. The deposition of mercury in throughfall and litterfall in the Lake Champlain watershed: a short-term study. *Atmos. Environ.* In Press.
- Scherbatskoy, T., J.M. Burke, A.W. Rea and G.J. Keeler. 1995. 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.* Soc. Environ. Toxicol. and Chem. In Press.
- Vasu, A.B. and M.L. McCullough. 1994. First report to Congress on deposition of air pollutants to the Great Waters. EPA-453/R-93-055. U.S. EPA Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

**Table 1:** Area and percent for total basin area of major land use classes in the Lake Champlain basin, based on aerial photography in 1973 (Budd and Meals 1994).

Classification:	Forest & Wetland	Agriculture	Urban	Surface Waters	Lake Champlain	Total Non-Lake	Total Basin
Area (ha):	1,322,506	567,262	55,840	75,111	113,000	2,020,719	2,133,719
Percent:	62%	27%	3%	4%	5%		

**Table 2.** Seasonal distribution of volume-weighted mean Hg concentration in precipitation, with weighted standard deviation in parentheses, number of events, precipitation amount and total Hg deposition, in 1993 and 1994 at the VMC field monitoring station in Underhill Center, VT. Seasons are defined as 22 Dec. to 20 Mar. (winter), 21 Mar. to 20 Jun. (spring), 21 June. to 22 Sept. (summer), and 23 Sept. to 21 Dec. (fall).

Season	Mean (ng/L)	Events (n)	Precipitation (cm)	Deposition ( $\mu\text{g}/\text{m}^2$ )
Winter 1993	4.4 (3.4)	26	17.7	0.87
Spring 1993	10.0 (5.9)	29	26.6	2.59
Summer 1993	11.1 (4.8)	35	38.8	4.32
Fall 1993	5.3 (3.2)	33	30.2	1.62
Winter 1994	4.5 (3.4)	26	18.7	0.84
Spring 1994	8.6 (4.8)	30	34.3	2.91
Summer 1994	7.8 (5.0)	32	39.6	3.18

**Table 3.** Seasonal distribution of particulate and vapor phase Hg concentration, with standard deviation in parentheses, and number of samples, in 1993 at the VMC field monitoring station in Underhill Center, VT. Seasons are defined as in Table 2.

Season	Particulate (pg/m <sup>3</sup> )	Samples (n)	Vapor (ng/m <sup>3</sup> )	Samples (n)
Winter 1993	16 (11)	24	2.21(0.34)	21
Spring 1993	10 (5)	26	2.16 (0.41)	26
Summer 1993	9 (4)	26	1.79 (0.75)	20
Fall 1993	10 (8)	24	1.62 (0.14)	22
Winter 1994	17 (8)	11	1.75 (0.14)	7
Spring 1994	9 (4)	13	1.74 (0.16)	12
Summer 1994	7 (3)	9	1.68 (0.42)	9

**Table 4.** Mercury chemistry of snowfall and snowpack during winter 1993-94, at the VMC field monitoring station in Underhill Center, VT.

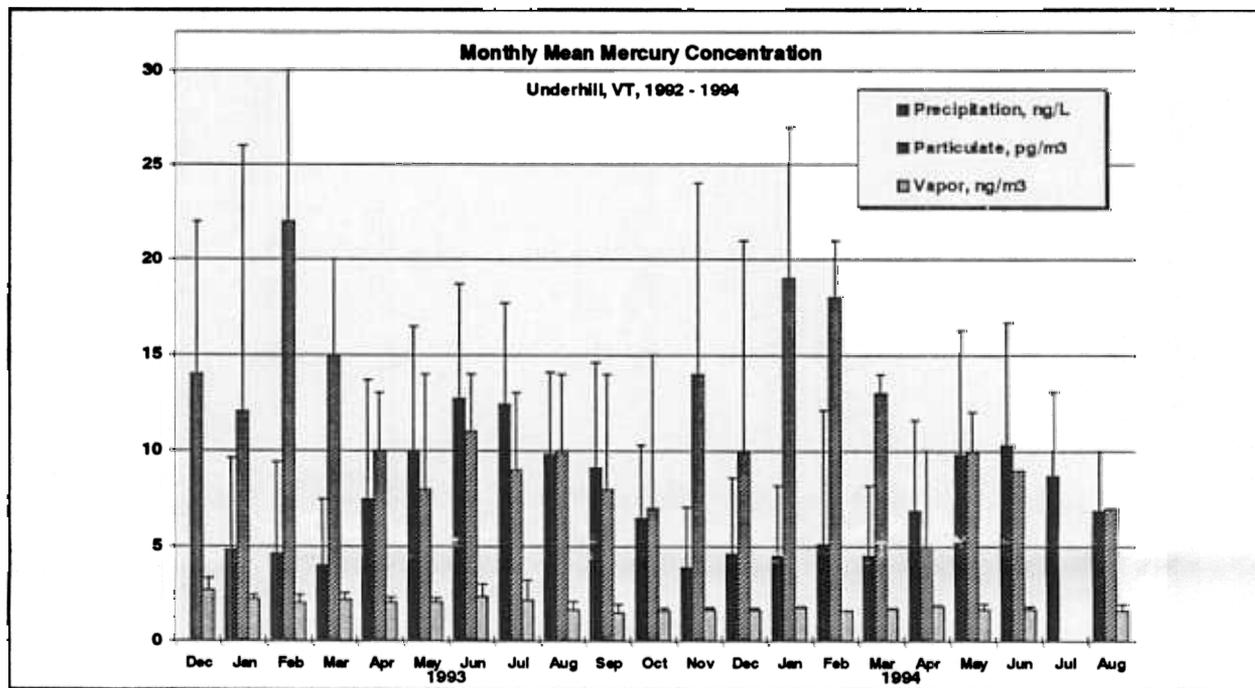
**SNOWFALL, 11/28/93 - 3/28/94**

	mean	min	max	total
amount (mm)	7.6	1	29	222
Hg concentration (ng/L)	5.3*	1.2	14.5	
Hg deposition ( $\mu\text{g}/\text{m}^2$ )	0.04	0.004	0.22	1.18

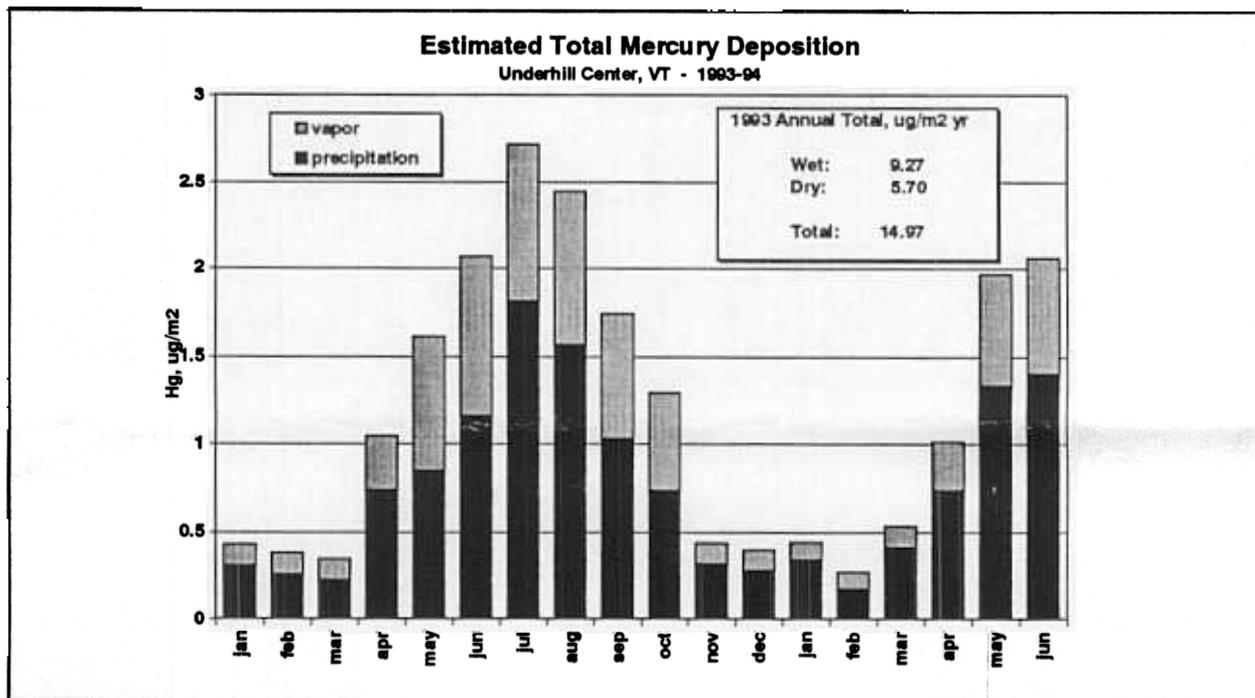
\* Volume Weighted Mean

**SNOWMELT, 3/24/94 - 4/14/94**

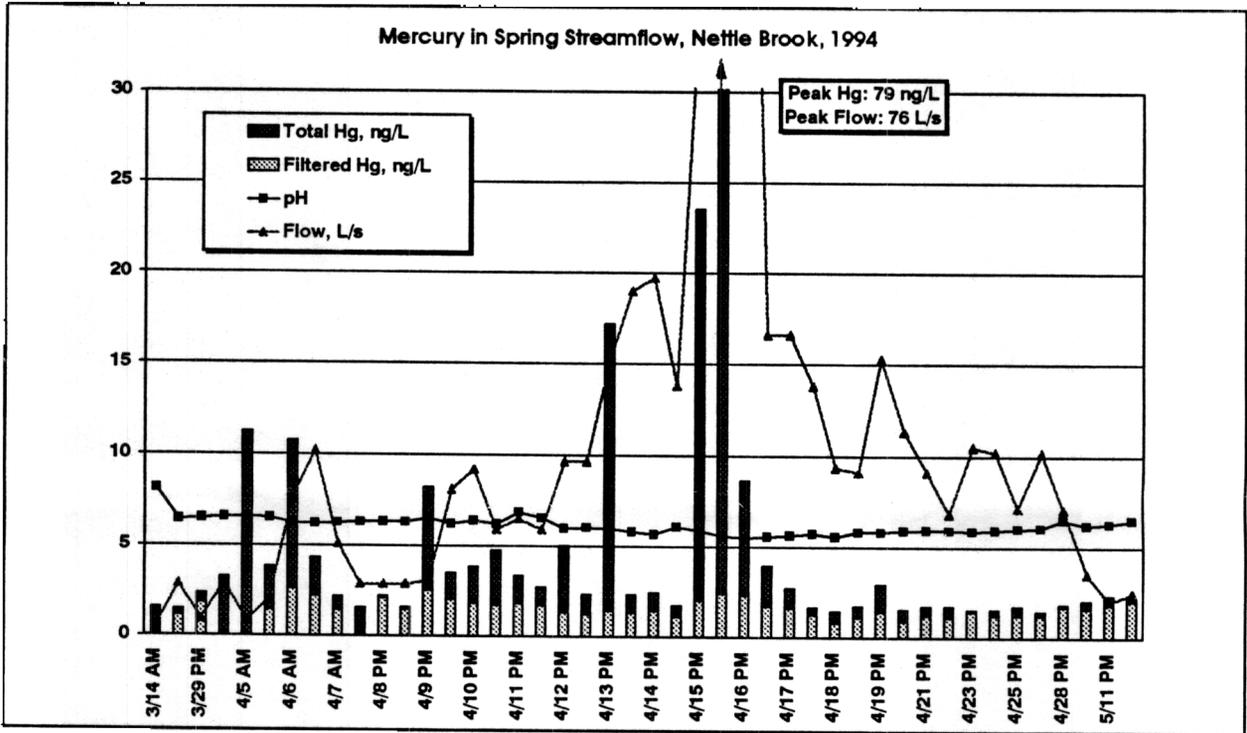
	mean	min	max
Total Hg (ng/L)	4.8	2.0	9.2
Filtered Hg (ng/L)	2.4	0.8	5.7



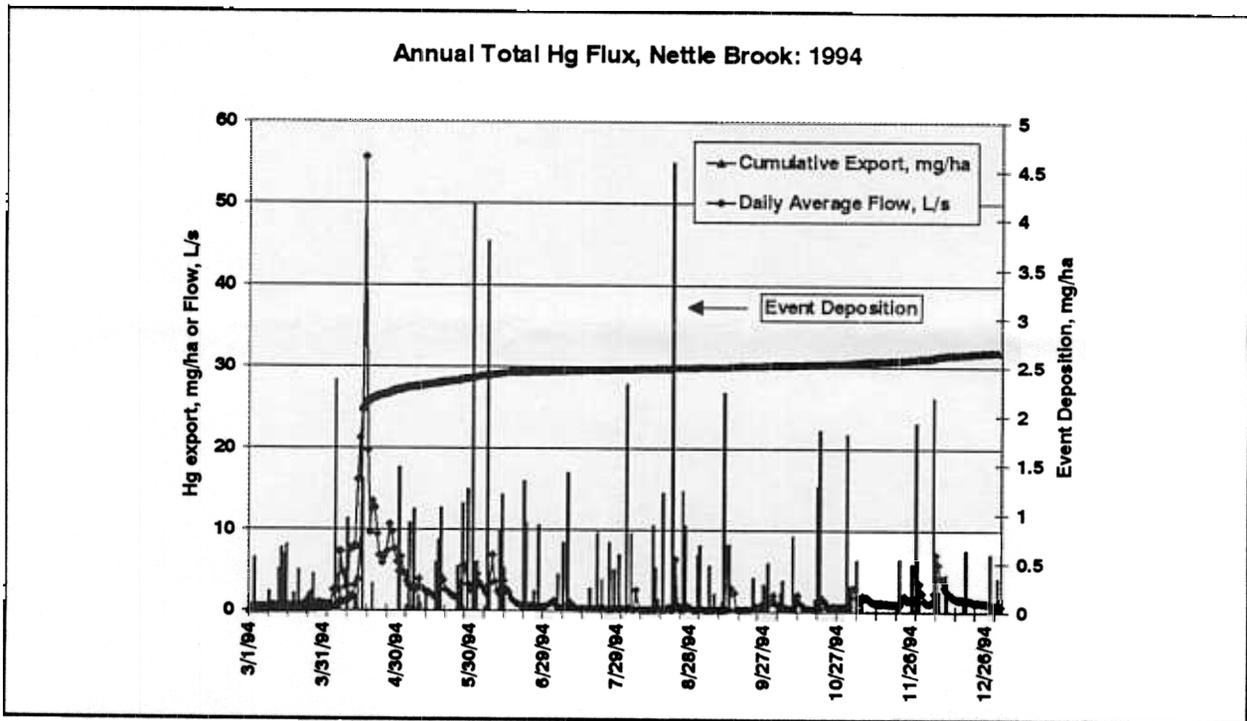
**Figure 1.** Monthly average Hg concentrations ( $\pm$  SD) in precipitation (volume weighted), particulate and vapor phases for December 1992 through August 1994 at Underhill Center, Vermont.



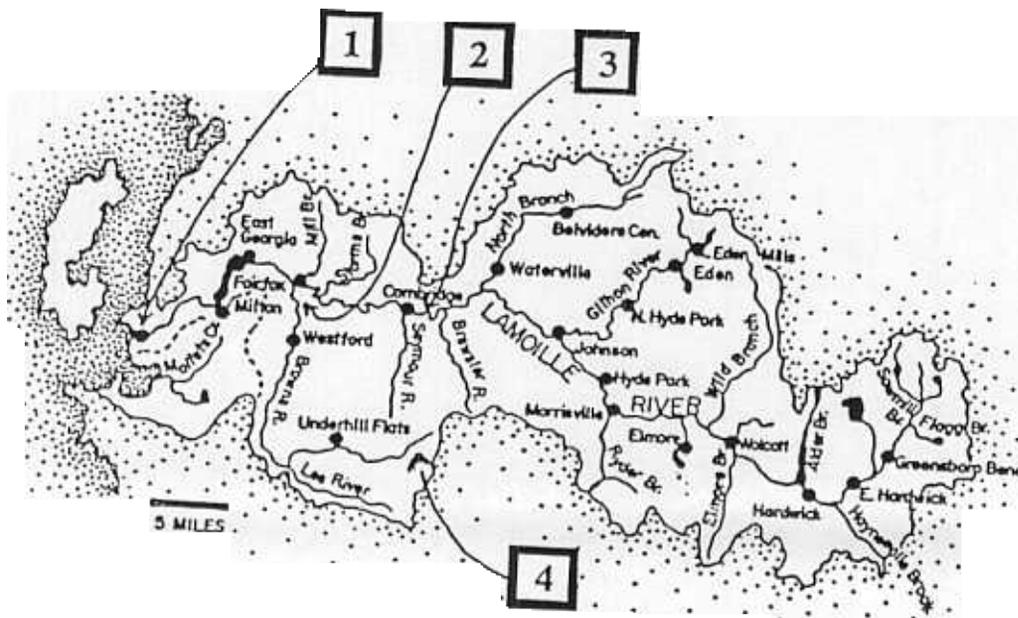
**Figure 2.** Wet and dry deposition of Hg from precipitation and estimated vapor deposition at Underhill Center, Vermont, in 1993 and 1994.



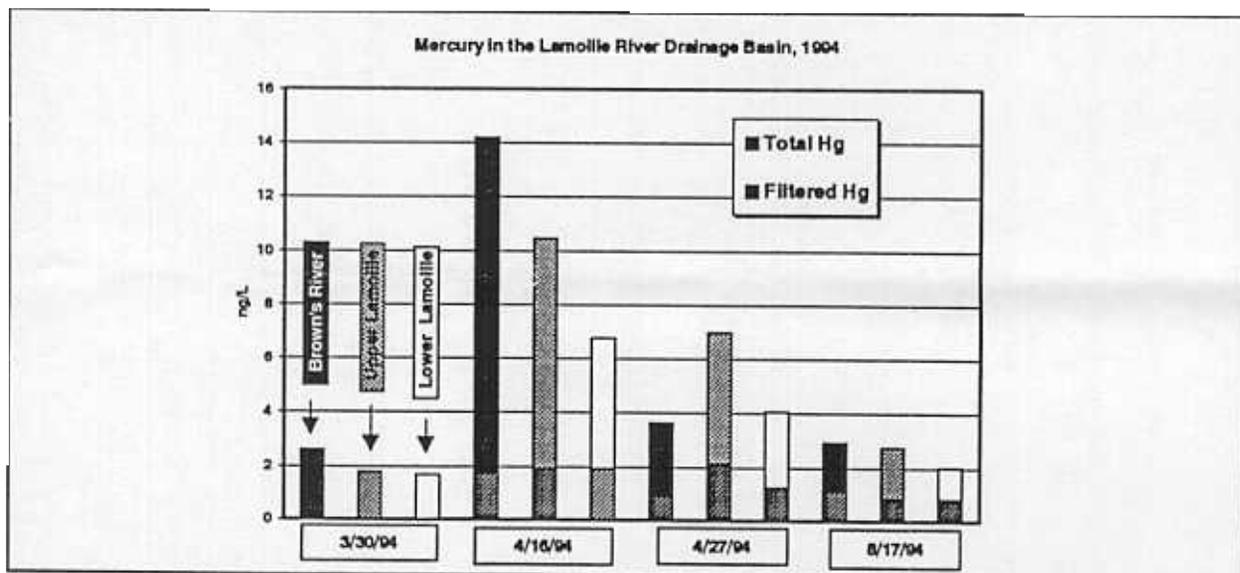
**Figure 3.** Streamflow, pH, filtered and total Hg during spring runoff at Nettle Brook in northern Vermont in March and April, 1994.



**Figure 4.** Cumulative Hg export (mg/ha) from Nettle Brook from March through December 1994, daily average flow (L/s), and event deposition.



**Figure 5.** Map of Lamoille River drainage basin in Vermont east of Lake Champlain, showing locations of sampling stations at West Milton (1), Brown's River (2), Jeffersonville (3) and Nettle Brook (4).



**Figure 6.** Total Hg in river water at three sites in the Lamoille River drainage basin in northern Vermont in 1994, showing filtered and total Hg fractions (only total Hg data for 30 March).

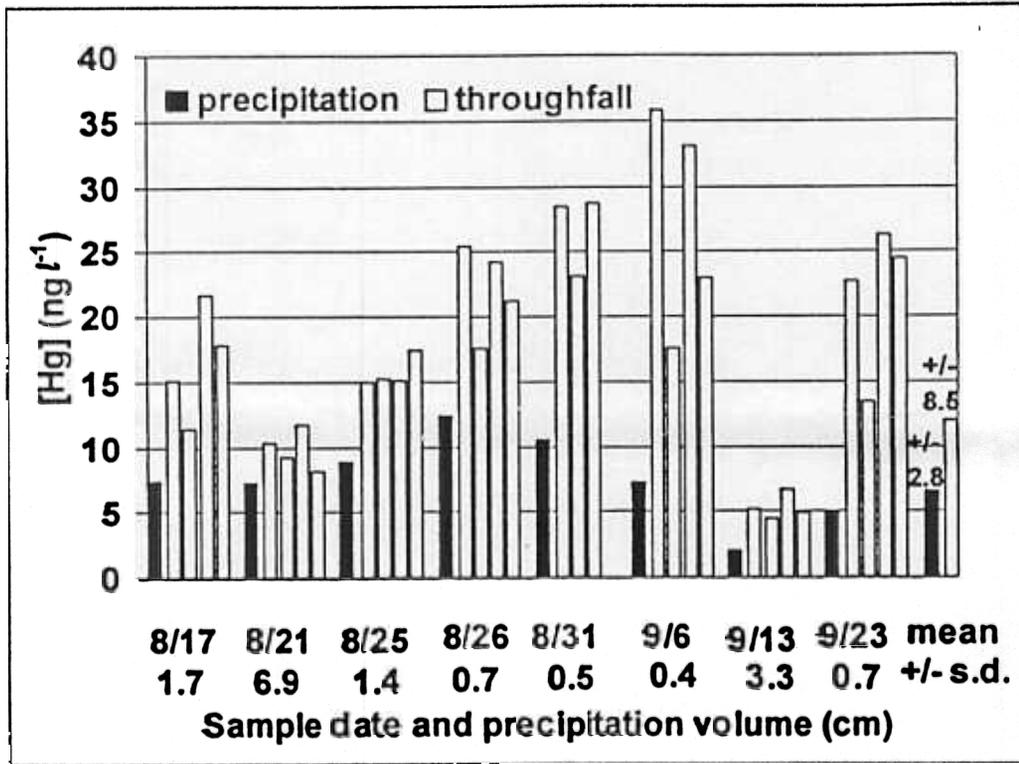


Figure Total Hg concentration (ng/L) precipitation throughfall also show precipitation volume) for each event for which throughfall was recorded August-September 99. The last two bars indicate all standard