

**Atmospheric Mercury Deposition
in the Lake Champlain Basin of Vermont
- 1993 -**

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Cooperators:

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Abstract:

A new research program to quantify mercury (Hg) deposition in the Lake Champlain Basin was initiated by the Vermont Monitoring Cooperative (VMC) in cooperation with the Lake Champlain Research Consortium, University of Michigan Air Quality Laboratory, and NOAA (National Oceanic and Atmospheric Administration). Monitoring of Hg in precipitation, vapor and particulate phases began 16 December, 1992 at the VMC air quality site at the Proctor Maple Research Center in Underhill (400 m elevation). Precipitation was collected on a daily/event basis using a wet-only precipitation collector, and vapor and particulate phases were collected in 24-hour air samples twice a week. Samples were shipped to the University of Michigan Air Quality Laboratory (UMAQL) where they were analyzed for total Hg by cold vapor atomic fluorescence spectrometry within 48 hours of collection in the field.

Results indicate that there are significant levels of Hg present at all times in all three phases. Mercury in precipitation ranged from 1.5-26 ng/L, with a volume-weighted mean of 8.3 ng/L for 1993; the highest concentrations occurred during the summer months. Deposition of total Hg in precipitation events averaged $0.07 \mu\text{g}/\text{m}^2$ during this period, with total deposition of $9.26 \mu\text{g}/\text{m}^2$ for 1993. Vapor phase Hg ranged from 1.2 to $4.2 \text{ ng}/\text{m}^3$, with a mean of $2.0 \text{ ng}/\text{m}^3$ during this period. Particulate phase Hg ranged from 1 to $43 \text{ pg}/\text{m}^3$, with a mean of $11.2 \text{ pg}/\text{m}^3$, with the highest concentrations occurring in the winter months.

Mercury in snowmelt-fed stream water was also measured in Harvey Brook, a small stream near the deposition monitoring site. Stream water concentrations were measured twice daily during snowmelt from 26-31 March, and ranged from 1.9 to 12.6 ng/L with concentrations during afternoon high flow being 2-4 times greater than during morning lower flow.

Introduction:

There is widespread concern that atmospheric sources of mercury may be responsible for increasing mercury burdens in Lake Champlain. 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 data for the Lake Champlain Basin. Currently there is a Vermont State Health Advisory against the consumption of Walleye from Lake Champlain due to mercury contamination. In addition, recent research supported by the VT Water Resources Research and Lake Studies Center has identified elevated levels of mercury and other metals in sediments in the lake. Little information exists on levels or behavior of mercury in forested ecosystems, but atmospheric and forest scientists are becoming increasingly concerned about the impacts of long distance transport of hazardous air pollutants including mercury into northern Vermont. 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. Furthermore, as mercury is a potent toxin to many organisms, its presence and behavior in forest soils, plants or waters is potentially of great concern. This program to monitor atmospheric mercury was established to address information needs of several groups: aquatic, terrestrial and atmospheric.

Objectives:

The goals of the mercury monitoring and research program include: (1) characterizing mercury deposition in precipitation, aerosol and vapor phases, (2) studying mercury transport and processing in a forested watershed (including snowmelt, stream chemistry and hydrology, and forest throughfall), and (3) supporting larger Lake Champlain issues (meso-scale modeling of pollutant deposition, trace metal toxicology, sediment accumulation, etc.).

Specific objectives for 1993 included: (1) monitoring mercury concentration in every precipitation event and twice-weekly vapor and particulate phase samples, and (2) measuring mercury concentration in a snow-melt fed stream in early spring.

Methods:

Precipitation samples were collected in a MIC-B (MIC Co., Richmond Hill, Ontario) wet-only precipitation collector located at the air quality monitoring station at the Proctor Maple Research Center (400 m elevation). This collector contains a large Teflon coated funnel for trace metal sampling, and was co-located with the other precipitation monitoring equipment (e.g., NADP. AIRMoN, see Cummings and Scherbatskoy, this volume) at this site. Samples were collected on a daily/event basis (samples were collected every morning that there was precipitation) and shipped by overnight courier to the University of Michigan Air Quality Laboratory (UMAQL) for analysis within 48 hours.

Vapor and particulate samples were collected every Wednesday and every sixth day as 24-hour air samples on gold-coated sand vapor traps and glass-fiber particulate filters, respectively; these were shipped on the day of collection to UMAQL for analysis.

During five days of peak snowmelt in early spring (26-31 March), stream water samples were collected twice daily from Harvey Brook, a small stream near the air quality monitoring site. Samples were collected in the early morning and late afternoon using the same type of sample bottles and analytical procedures as for precipitation.

All samples were analyzed for total elemental mercury by cold vapor atomic fluorescence spectrometry (CVAFS). Ultra-clean sampling, handling and storage techniques were used throughout all procedures. In the field, this entailed wearing particle-free gloves to handle sample bottles and filter packs, and triple bagging all samples. Analysis and sample bottle preparation at UMAQL was conducted in a Class 100 clean lab. Twenty percent of the samples were analytical blanks for quality assurance purposes. Analytical accuracy was within 5% of known standards and precision error was less than 8%. No Hg speciation was performed, so all data represent total Hg measurements.

Results:

Atmospheric Deposition.

Mercury concentrations in the three principle phases (precipitation, vapor and particulate) are summarized in Figure 1. For the year, volume-weighted average precipitation Hg concentration was

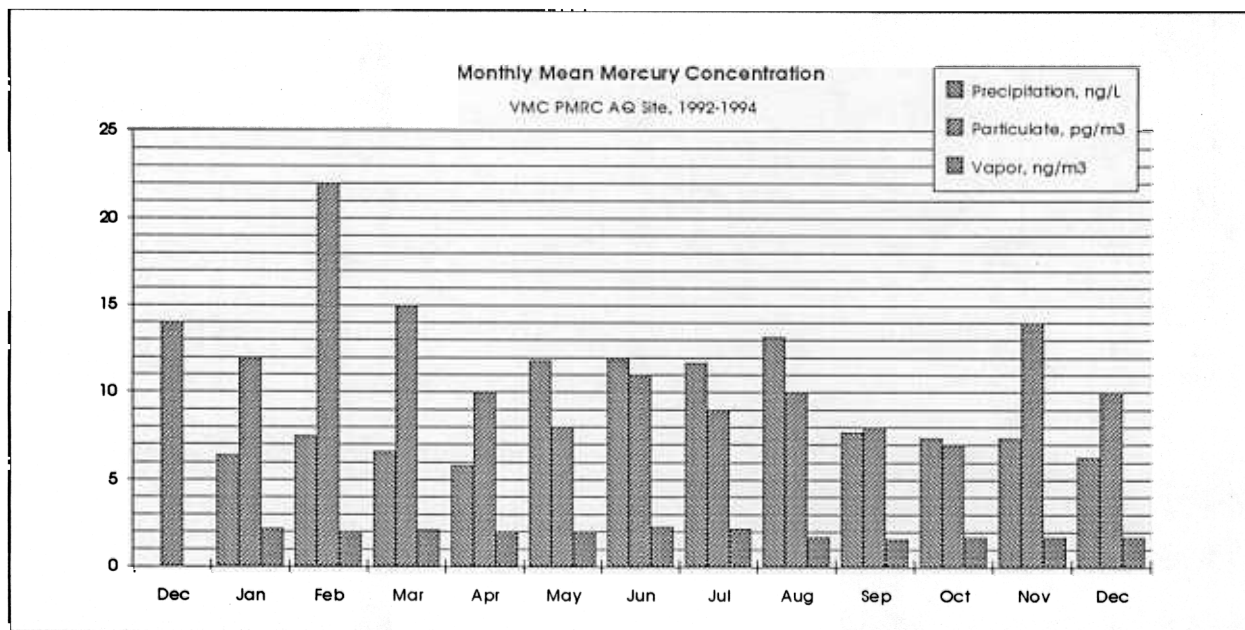


Figure 1: Average monthly mercury concentrations in precipitation, particulate and vapor phases in December 1992 and all of 1993.

8.3 ng/L, with the highest concentrations occurring in the summer months; vapor phase Hg was relatively constant throughout the year, averaging 2.0 ng/m³. Particulate Hg concentration was greatest in the winter months, and averaged 11.2 pg/m³ for the year. These data are comparable in magnitude and trend to values for northern Michigan, where other sites in the network are operated (Burke et al 1994, Hoyer *et al.* 1994). Mercury deposition in precipitation was also greatest in the

summer months, due to high concentration and high precipitation amount. Total annual Hg deposition was $9.26 \mu\text{g}/\text{m}^2$, distributed as shown in Figure 2.

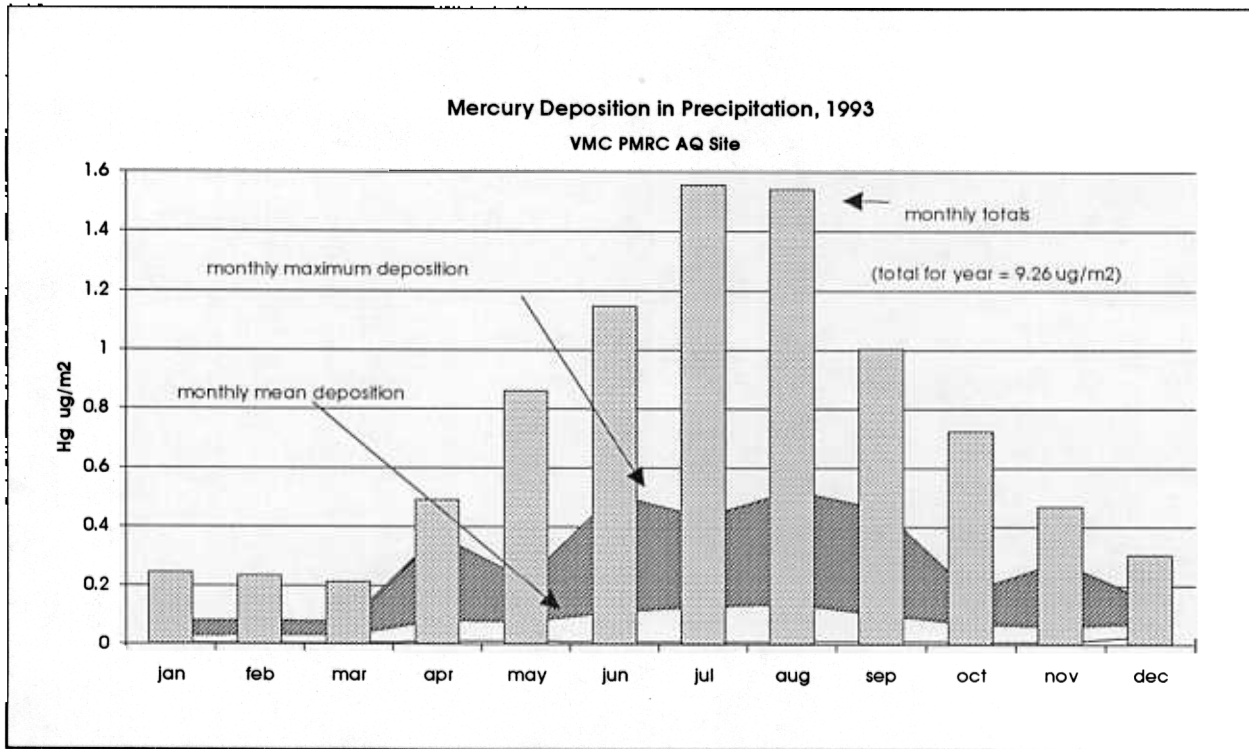


Figure 2: Mercury deposition in precipitation, showing monthly totals as bars, and maximum and minimum deposition for each month in 1993.

Surface Water Chemistry.

Stream water Hg concentrations during snowmelt fluctuated diurnally, being higher in the afternoon samples when stream flow rate was greater (Figure 3). No attempt was made to quantify the flow rate, but observations at the time of collection indicated substantially greater flow during the warm afternoons and lower flow during the cold mornings. Air temperature was above freezing during all of this period, ranging between 2 and 16 °C. Stream water Hg concentrations varied during this period between 2 and 12 ng/L, with an average of 6.1 ng/L. During this period, NO₃ concentrations increased slightly (mean of 1.8 mg/L) and SO₄ concentrations declined slightly (mean of 5.9 mg/L).

Discussion:

Atmospheric Hg vapor concentrations varied little during the year, and were comparable to measured vapor concentrations in rural Michigan, the Great Lakes region and New York, about 2 ng/m³ (Burke *et al.* 1994). Particulate Hg, however, was considerably greater in the winter months (~15 pg/m³) than in the summer months (~9 pg/m³), suggesting possible wintertime increases in

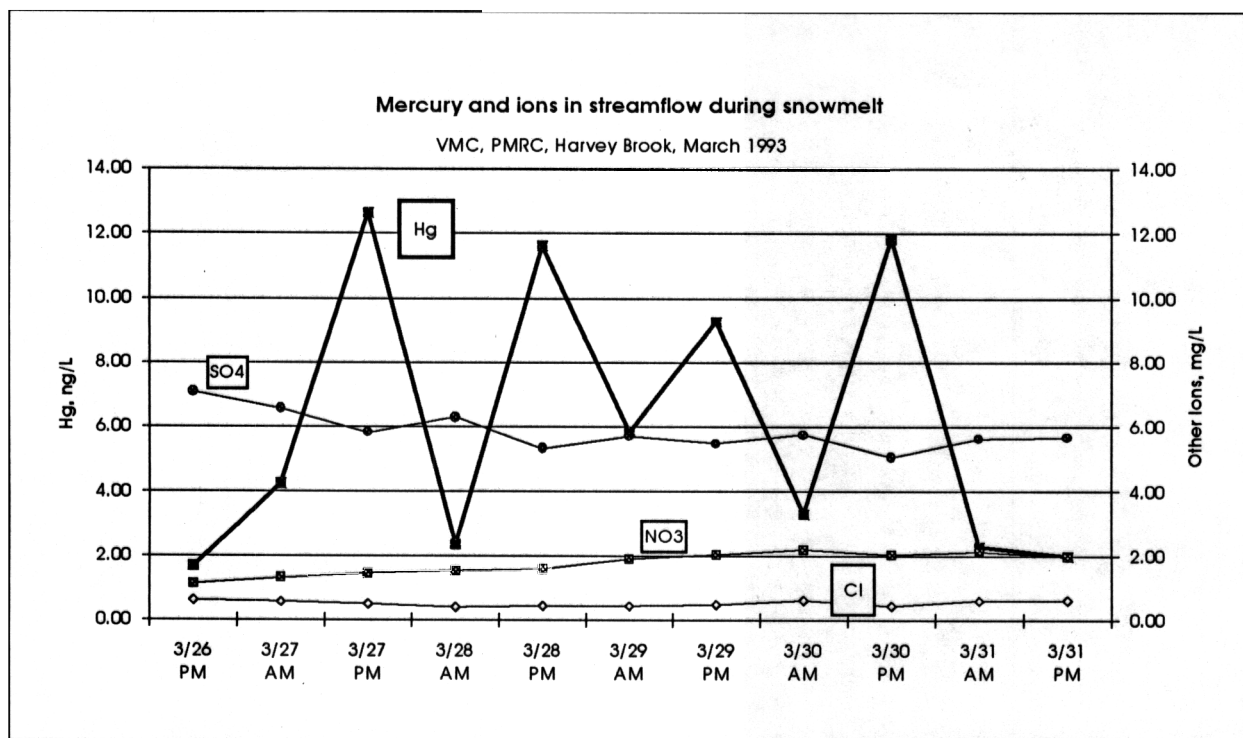


Figure 3: Twice-daily measurements of stream water during five days of spring snow-melt for total Hg, SO₄, NO₃ and Cl.

sources. A similar trend toward higher concentrations in winter was also seen for Hg particulate in Michigan (Burke *et al.* 1994). Other trace metals - notably As and Se, usually associated with coal combustion emission signatures - have also been observed to increase in winter aerosol concentrations at PMRC and in Michigan.

Precipitation Hg concentrations were significantly greater in the summer months (~11 ng/L) than in the winter months (~5 ng/L), but without additional data it is difficult to determine if this is a normal trend related to temperature and source emission patterns. Nonetheless, precipitation Hg deposition was also considerably greater in the summer months, due to the combined effects of higher concentration and higher amounts of precipitation than in the winter. During the summer months, more than 1 $\mu\text{g}/\text{m}^2$ Hg per month was deposited, compared to about 0.2 $\mu\text{g}/\text{m}^2$ Hg per month during the winter. The total deposition for the entire year, 9.26 $\mu\text{g}/\text{m}^2$ Hg, was comparable to that of rural sites in Michigan (range 6.2 - 9.9 $\mu\text{g}/\text{m}^2$, Burke *et al.* 1994).

Typical total Hg concentrations tend to be around 0.5-2 ng/L in many waters (Porcella *et al.* 1991), and appear to be in the 2 ng/L range during low flow for the stream sampled in this study. In the afternoon stream samples, however, Hg concentrations were 2 to 4 times greater than during base flow, increasing to as much as 12 ng/L. These increases appeared to be associated with diurnal increases in stream flow rate. Because Hg complexes strongly with organic matter, this increase could be partly due to increased suspension of Hg-bearing organic matter during increased flow. Increased Hg concentrations could also be caused by afternoon snowmelt adding higher concentrations of Hg to the stream. Without detailed information on snowpack chemistry, it is difficult to resolve this question. In either case, this would result in significantly increased flux of Hg to downstream

communities during these periods. We have not actually estimated Hg fluxes in the stream system because of the lack of flow data.

Although the variation in stream SO₄ concentration appears small, there was a pronounced negative correlation ($r=-0.61$) between SO₄ and Hg during snowmelt (Figure 3). This was probably caused by a flow-related dilution of stream SO₄ (rather than an interaction between Hg and SO₄), but because this pattern was not apparent for NO₃ or Cl, it could suggest a chemical relationship between SO₄ and Hg.

At this time, no information is available about the forms of Hg in precipitation or stream samples, although it is assumed that only 2-10% of the Hg in precipitation is in the methyl form, the remainder being inorganic (Bloom and Watras 1989). In Adirondack lakes typical total Hg concentrations range from 0.8 to 5.3 ng/L, with about 10% being methyl Hg (Driscoll *et al.* 1994). There are no comparable Hg data available for uncontaminated streams. Although methyl Hg concentrations are usually relatively low in waters, it is this form that is highly toxic and accumulates in animal tissues. These levels in lake water yielded from 0.2 to 1.2 $\mu\text{g/g}$ Hg in tissues of yellow perch, depending on fish age (the US FDA action level for Hg is 1 $\mu\text{g/g}$). Concentrations of total Hg in Harvey Brook during our snowmelt sampling period were many times greater than the Adirondack lakes, suggesting possibilities for significant accumulation and toxic effects on stream biota. More information on the form of Hg (inorganic, methylated, particulate, etc.) and on stream water chemistry (pH, DOC, etc.) is needed to assess the likelihood of these effects, but these data indicate the need for further study of Hg concentrations in snowmelt and stream waters.

Future Plans:

In 1994 we will continue monitoring precipitation, vapor and particulate phase atmospheric mercury, although we anticipate reducing the vapor and particulate sampling to weekly. In addition, we will conduct regular sampling of stream water for mercury and major ions at the new continuously gauged weir on Nettle Brook in the Stevensville Brook watershed. This work will also include intensive studies of mercury chemistry during spring snow-melt. Associated with this will be analysis of mercury in accumulated snowpack and snowpack melt water. We will also conduct limited synoptic sampling at several sites in the Lamoille River drainage system. Finally, we hope to obtain funding to conduct an intensive study of mercury chemistry in forest throughfall. These studies are designed to continue our basic monitoring of atmospheric mercury deposition and to build toward understanding the processes controlling mercury deposition, transport, transformation and accumulation in the watersheds and streams of the Lake Champlain Basin.

Regional Context:

This work was designed primarily to provide information about Hg deposition patterns, transport and transformation processes in the Lake Champlain Basin. The precipitation, vapor and aerosol monitoring are coordinated with ongoing mercury monitoring in the Great Lakes Region operated by UMAQL (Hoyer *et al.* 1994). Data from this study are used in regional analyses of mercury transport and deposition patterns in northeastern North America, and in meso-scale analysis of hazardous air pollutant deposition in the Lake Champlain Basin being conducted by the NOAA

Air Resources Laboratory. As part of the effort to assess toxics deposition in the Great Waters of the US, this work provides valuable data on Hg deposition and ecological processing in this region. In addition, these data represent an important baseline database, and support research on mercury patterns and toxicology in Lake Champlain by scientists in the Lake Champlain Research Consortium.

Acknowledgements:

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