Paleostratigraphy of Mercury in Branch Pond, Sunderland, VT

Submitted to the Vermont Monitoring Cooperative

by

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Executive Summary

In response to problems associated with mercury (Hg) in the freshwater environment, there is increasing interest in understanding the relative magnitude of present and historical atmospheric mercury deposition to north-temperate lakes. Improvement in the Hg situation on VT lakes will necessitate reductions in discharges and emissions of Hg both locally, and nationally. Paleolimnologically-derived estimates of atmospheric Hg deposition may serve as inexpensive monitors of anticipated reductions in Hg emissions. The purpose of this report is to present results of a paleolimnological analysis performed at Branch Pond, Sunderland, VT to identify the signature of atmospheric Hg deposition to the lake's watershed.

In August of 1999, a core was acquired from the sediments of Branch Pond, Sunderland, VT, in the Lye Brook Wilderness area. This core was dated by ^{210}Pb, and analyzed for a variety of parameters relating to the deposition of mercury (Hg) to the lake sediments. This analysis was undertaken with support from VMC, in conjunction with the USEPA-sponsored REMAP Assessment of Mercury in Lake Sediments, Waters and Biota of VT and NH Lakes Project.

The general pattern of Hg fluxes to the sediments of Branch Pond indicate increasing atmospherically driven Hg deposition, beginning by the year 1850. This finding is consistent with other lakes studied by the REMAP project, as well as with findings of other studies. Hg fluxes to the lake continued to increase throughout the period 1850 to 1980. A decline in flux to the sediments is apparent in recent years.

The signals in fluxes of Hg to Branch Pond sediments are not as clear as for other lakes. There is evidence from the ^{210}Pb-inferred sedimentation record, as well as from sediment organic content, that the delivery of Hg to the sediments of Branch Pond has been enhanc Tw (t5mge f -0.23, and Tj 0 9 -4H9tncildern2 Tc -0.427 Tc 0
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Introduction:

In response to problems associated with mercury (Hg) in the freshwater environment, there is increasing interest in understanding the relative magnitude of present and historical atmospheric mercury deposition to north-temperate lakes. Measurements of direct atmospheric deposition of Hg are expensive, and are only being made at a handful of northeastern locations. Improvement in the Hg situation on VT lakes will necessitate reductions in discharges and emissions of Hg both locally, and nationally. Paleolimnological proxies for estimating atmospheric Hg deposition may serve as inexpensive 'monitors' of Hg deposition to the northeastern landscape. The purpose of this report is to present results of a paleolimnological analysis performed at Branch Pond, Sunderland, VT to identify the signature of atmospheric Hg deposition to the lake's watershed.

Paleolimnology is a tool which came of age largely in the 1980's, and which has been successfully used to infer the historical trophic state and acidification status of lakes (Ouellet and Jones, 1983, Oldfield and Appleby, 1984, Charles and Norton, 1986, Charles and Whitehead, 1986). Recent attention has been focused on inferring historical deposition of Hg to lakes, which has increased over the previous 100 years (Swain and Engstrom 1992). Results from large studies of lakes across North America suggest that declines have occurred in the previous 10 years in the midwestern lakes, but that deposition continues to increase for lakes west of the midwestern industrial centers, and in arctic regions (Engstrom and Swain, 1996, Hermanson, 1998, and Lockhart et al. 1998). Reductions are attributed to diminished Hg point source emissions. Most recently, archived Adirondack sediment samples from the PIRLA project (Charles and Whitehead, 1986) have been analyzed for Hg (Lorey and Driscoll, 1998). These analyses were used in part to compare sediment-inferred Hg deposition to measured atmospheric Hg deposition. The authors found that their core-derived estimates of modern atmospheric deposition of Hg were in good agreement with direct measurements, which gave confidence that core-derived estimates from deeper in the core could be used to estimate historical atmospheric deposition.

The Northeast States and Eastern Canadian Provinces Mercury Study (NESCAUM, 1998) recommends that "data on Hg emissions and deposition be statistically analyzed ... to enhance understanding of the air/water interrelationship." To this end, USEPA has entered into a cooperative agreement with the VTDEC to coordinate a Vermont-New Hampshire wide assessment of Hg and methylHg in sediments and waters of 90 lakes, following a regional EPA-EMAP (REMAP) sampling design. In conjunction with this project, a total of 12 paleolimnological sediment cores are to be collected, dated using ^{210}Pb, and analyzed for total Hg at 15 depths downcore. The REMAP project is described in detail by Kamman et al. (1997).

In 1999, VMC supported the inclusion of a 13th lake, Branch Pond, in the Lye Brook Wilderness into the REMAP paleolimnology set. With respect to biogeochemistry, the critically acidic (Kellogg, 1998) Branch Pond has a variety of factors which the literature suggests should enhance methylation of Hg (Kellogg, 1998, N. Kamman, unpublished data). Among these are low pH, high dissolved organic carbon (DOC), anoxic hypolimnion, and large adjacent wetlands. Discussion regarding the specifics on how methylation is mediated by these parameters is beyond the scope of this report. A 19 year record of monitoring relating to acidification and biological conditions exists for Branch Pond (Kellogg, 1998; Kamman, 1998). Branch Pond was included in the early 1980's PIRLA project (Charles and Whitehead, 1986), but detailed results from that effort are not available as of this writing.

Methods:

On August 19, 1999, a sediment core was acquired from the deep hole of Branch Pond (43º04.84' N, 073º01.19' W), o

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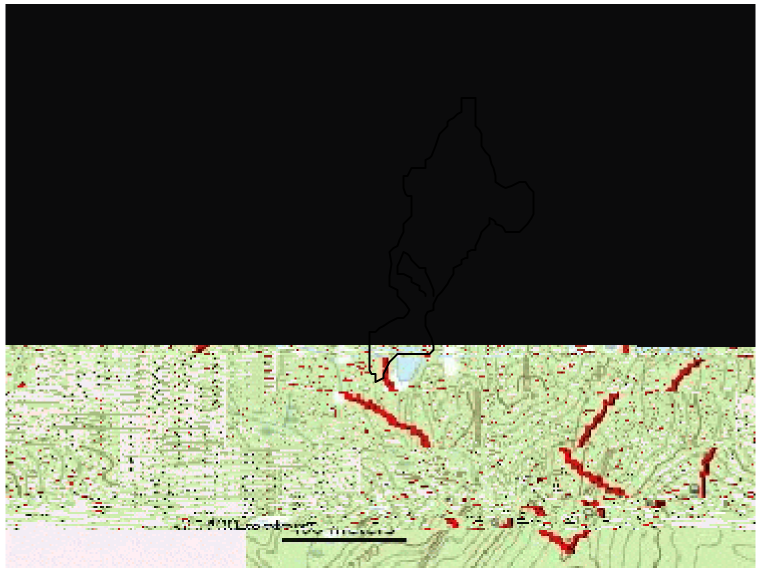
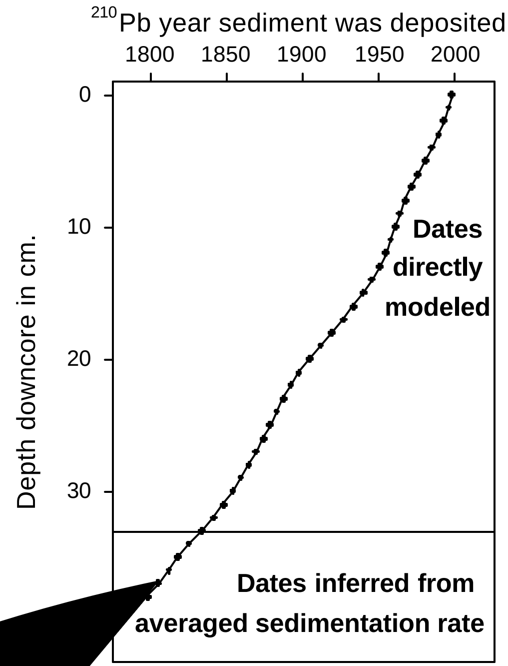


Figure 1. Locator map for Branch Pond, Sunderland, VT, showing sediment coring location (**!**), and the watershed boundary.



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decline, there was a small spike at 17 cm (1927). This spike was clearly reflected in the concentration profile as well.

Comparison with other Studies:

The flux rates measured in this analysis are elevated in relation to the remaining REMAP lakes, and are also elevated in relation to those measured for a set of Adirondack lakes by Lorey and Driscoll (1998), and for Wisconsin and Minnesota lakes cored by Engstrom and Swain (1996). This likely reflects the very high concentrations of Hg existing in the lake sediments as compared to lakes in these other studies. At face value this might call into question the validity of the measurements made for Hg. However, internal QC checks (including standard reference material) performed by the DEC laboratory in the course of this study produced excellent results. These high concentrations are probably the result of a high delivery of Hg to the lake from the very poorly buffered watershed, and nearby littoral wetlands, phenomena shown by many studies which are reviewed by Kamman (1998b). Table 1 provides a comparison of Branch Pond Hg concentrations and fluxes to the remainder of the REMAP study set.

In addition, the modern and peak flux ratios (ratio of modern or peak to baseline fluxes) for Branch Pond are 3.36 and 4.66 respectively, and these compare very well with the above mentioned studies as well as for the remaining REMAP set.

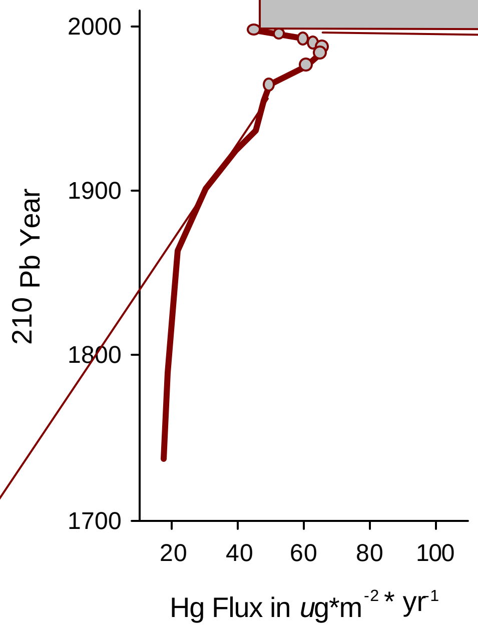
Table 1. Comparison of Hg concentrations and fluxes between Branch Pond and lakes in the REMAP paleolimnology study set.

Lake	Mean Hg ($ug \cdot g^{-1}$ d.w.)	Mean sedimentation rate ($g \cdot cm^{-2} \cdot yr^{-1}$)	Mean HgT flux (ug $Hg \cdot m^{2} \cdot yr^{-1}$)
All lakes (N = 11)	0.258	0.016	40.08
Branch Pond	0.44	0.018	74.06

Discussion:

The literature indicates that a large component of the increases in flux observed for lake sediment profiles is attributable to atmospheric deposition. This signal is superimposed over that of Hg released from land use activities in the watershed (Engstrom and Swain, 1996; Hermanson et al., 1998; Lockhart et al., 1998; Lorey and Driscoll, 1998). Given data from only one lake, it is difficult to separate the effect of atmospheric deposition from that of watershed loading due to land use activities (S. Norton, Univ. of Maine, pers. comm.). Therefore it is useful to compare Hg flux profile to those within other similar lakes.

A generalized pattern of Hg flux to sediments is apparent in north-temperate lakes, as described by Engstrom and Swain (1997), Lorey and Driscoll (1998) and others. This pattern is also evident for nearly all lakes analyzed for the REMAP paleolimnology study set (N. Kamman, unpublished data), and for several lakes in Maine (S. Norton, pers. comm.). For lakes which have experienced only minimal watershed disturbance, there exists a pattern of slowly increasing fluxes above baseline levels, trending towards a peak at the period 1975 to 1980. Many cores show a subsequent decline, which Engstrom and Swain (1996) attribute to real reductions in atmospheric Hg deposition.


2000
1900
1800
1700
210 Pb Year
20
40
60
80
100
Hg Flux in ug*m-2 * yr-1

time was likely flushed from the watershed during cutting.

From 1954 to 1971, Hg fluxes remained stable during a period of decreasing sedimentation, indicating continually increasing atmospheric flux. Aerial photography from 1962 shows the watershed as being completely forested, with the network of logging roads evident on the 1942 photography regrown. The 1974 photography identifies the construction of the first major improved dirt road to penetrate the Branch Pond watershed and allow public access to the pond from the Arlington-Stratton (‘Kelly Stand’) Road. This road was drastically widened and improved in recent years, and this activity is evident in the slight sedimentation pulse which occurred in the mid 1980's. This activity and resulting watershed disturbance likely released some Hg which was stored in that section of the watershed, thus masking the expected reduction in fluxes of atmospherically deposited Hg which are idealized by the Wallingford Pond flux profile (Figure 4). Finally, in present times, there are decreases in Hg fluxes based on the top centimeters, but these should be interpreted cautiously since surficial core sediments are prone to disturbance during sampling.

Conclusions:

Fluxes of Hg to Branch Pond are driven largely by atmospheric deposition, but mediated by watershed-based activities. ^{210}Pb-inferred sedimentation rates suggest that prior land-use activities played a large part in accelerating the delivery of Hg to the sediments of Branch Pond. Based on this analysis, it can be reasonably suggested that Branch Pond is biogeochemically sensitive to Hg accumulation, and accordingly, to bioaccumulation of Hg up the trophic chain.

Hg concentrations in and fluxes to the sediments have been elevated above what would be considered baseline since at least 1850. Across the REMAP set, and to a lesser degree in Branch Pond itself, there exists evidence of declines in modern Hg flux rates. These declines may be linked to the reduction in atmospheric deposition of Hg across the landscape. Evidence from the Branch Pond core suggests that, should these atmospheric improvements continue, surficial sediment Hg concentrations would continue to decline. Over the long term, this may result in a reduced source of both hypolimnetic and watershed-Hg available for methylation and subsequent bioaccumulation.

Recommendations:

This analysis shows that Hg fluxes to the sediments of Branch Pond are high in relation to other lakes in the REMAP paleolimnology study set. This is most likely attributable to enhanced delivery of Hg from the Branch Pond watershed. Branch Pond is the only lake to be cored and analyzed for Hg in the Lye Brook Wilderness area. Several lakes exist in and near the Lye Brook Wilderness which would serve as excellent sites to perform additional Hg core analyses. Bourn Pond, Stratton Pond, Grout Pond, and Beebe Pond are all presently forested, and given their proximity to each other, were all very likely subjected to similar historic land uses.

The present research would be enhanced by coring these lakes, dating the sediments, analyzing them for Hg and for the stable isotopes ^{13}C and ^{15}N. Such analyses would permit more robust inferences as to the provenance of the materials which constitute the sediments, and thus clarify the relative importance of land use in interpreting the signal of atmospheric Hg deposition across the Lye Brook region. From the standpoint of developing a paleolimnological proxy for estimating atmospheric Hg contributions to the Lye Brook region, the combined results of several lake cores would be extremely useful, since they would permit direct estimates of current and historical localized Hg deposition rates.

References:

Charles, D.F. and D. Whitehead. 1986. The PIRLA Project: Paleoecological Investigations of Recent Lake Acidification. Hydrobiologia 143: 13-20.

Charles, D. F. and S. Norton. 1986. Acid Deposition: Long-Term Trends. National Research Council, Committee on Monitoring and Assessment of Trends in Acid Deposition. National Academy Press. Washington, D.C. 506pp.

Driscoll, C.T., C. Yan, C. L. Schofield, R. Munson, J. Holsapple. 1994. The Role of Dissolved Organic Carbon in the Chemistry and Bioavailability of Mercury in Remote Adirondack Lakes. Wat. Air Soil Poll. 80: 499-508

Engstrom, D. B., and E.B. Swain. 1996. Recent Declines in Atmospheric Mercury Deposition in the Upper Midwest. Environ. Sci. Technol. 31:960-967.

Hermanson, M. 1998. Anthropogenic Mercury Deposition to Arctic Lake Sediments. Wat. Air Soil Poll. 101: 309-321.

Kamman, N., R. Estabrook, and R. Thompson. 1997. Quality Assurance Project Plan, Assessment of Mercury in Hypolimnetic Lake-bed Sediments of Vermont and New Hampshire. A REMAP Project. Vermont Department of Environmental Conservation. Waterbury. (Also available at http://www.anr.state.vt.us/water1.htm).

Kamman, 1998. Biocriteria Development for Vermont Lakes-Pilot and Field Phases. Project Summary, April, 1998. Vermont Department of Environmental Conservation. Waterbury. (Also available at http://www.anr.state.vt.us/water1.htm).

Kamman, 1998b. Inputs, Methylation, Transformation, and Historical Accretion of Mercury in Northern Freshwater Lakes. A Critical Review of Select Scientific Literature, and Comment on the Current Direction of New England Freshwater Mercury Research. http://www.anr.state.vt.us/dec/waterq/hgreview.pdf. URL Last updated 3/2000.

Kellogg, J. and H. Pembrook. 1997. Vermont Acid Precipitation Program, Long-term Lake Monitoring. Vermont Department of Environmental Conservation. Waterbury.

Lockhart, W.L., P. Wilkinson, B. Billeck, R. Danell, R. Hunt, G. Brunskill, J. Delaronde, and V. StLouis. 1998. Fluxes of Mercury to Lake Sediments in Central and Northern Canada Inferred from Dated Sediment Cores. Biogeochem. 40: 163-173.

Lorey, P. and C. Driscoll. 1998. Historical Trends of Mercury Deposition in Adirondack Lakes. Environ. Sci. Technol. 33: 718-722.

NESCAUM - Northeast States for Coordinated Air Use Management, 1998. Northeast States and Eastern Canadian Provinces Mercury Study. Boston, Mass.

Oldfield, F. and P. Appleby. 1984. Empirical Testing of ^{210}Pb Dating Models for Lake Sediments, *in* Lake Sediments and Environmental History. Univ. of Minnesota Press. Minneapolis.

Ouellet, M. and H. Jones. 1983. Historical Changes in Acid Precipitation and Heavy Metals Deposition

Originating from Fossil Fuel Combustion in Eastern North America as Revealed by Lake