



Deconstruction of Historic Mercury Accumulation in Lake Sediments, Northeastern United States

ETHAN PERRY,¹ STEPHEN A. NORTON,^{1,*} NEIL C. KAMMAN,² P. M. LOREY³ AND CHARLES T. DRISCOLL³

¹*Department of Earth Sciences, 5790 Bryand Global Science Center, University of Maine, Orono, Maine, USA 04469-5790*

²*Vermont Department of Environmental Conservation, 103 S. Main 10N, Waterbury, VT, USA 05671-0408*

³*Department of Civil and Environmental Engineering, 220 Hinds Hall, Syracuse University, Syracuse, NY, USA 13244-1190*

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Abstract. Total atmospheric contribution of mercury (Hg_T) to lake sediment was estimated using ^{210}Pb -dated sediment cores. Algorithms based on estimates of lake and watershed processes were applied to more accurately assess anthropogenic contributions of Hg to the environment and Hg_T . Factors addressed include: lake-specific background accumulation rates of Hg (Hg_B), variability of sediment accumulation rates that caused variation in Hg accumulation during the last 100–150 years (Hg_V), and variable flux of anthropogenic Hg from the atmosphere (Hg_A). These fluxes were normalized for sediment focusing using a regional, unsupported ^{210}Pb correction factor to yield $Hg_{A,F}$. Time series maps of $Hg_{A,F}$ allow for comparison across time and space, and are provided for 1900, 1950, 1975 and 1990 across eastern New York and New England, USA. Deconstruction algorithms reduce inter-/intra-lake variability in Hg accumulation rates and improve temporal coherence. $Hg_{A,F}$ started to increase near the end of the 19th century to a maximum between 1970 and 1990, depending on the lake. Maximum Hg_T across the region ranges from 27.1 to 175 $\mu g/m^2$ year. Maximum $Hg_{A,F}$ ranged from 10.4 to 66.3 $\mu g/m^2$ year. The timing of $Hg_{A,F}$ declines in response to decreased atmospheric deposition may be controlled by in-lake and in-watershed storage and transport of Hg-bearing sediment.

Keywords: ^{210}Pb ; anthropogenic mercury; atmospheric deposition; focusing; lake sediment; mercury; paleolimnology; peat; total mercury

Introduction

Mercury (Hg) is a naturally occurring element that undergoes long-range atmospheric transport. Emissions of Hg occur as elemental Hg (Hg^0)

which has a relatively long atmospheric residence time (0.5–3 years) and consequently, a potential for hemisphere-wide transport (Schroeder and Munthe, 1998). Mercury is also released as reactive gaseous and particulate Hg, both of which have shorter atmospheric residence times. Elemental Hg is oxidized to Hg^{2+} in the atmosphere. Deposition occurs by impaction and adsorption

*To whom correspondence should be addressed:
Tel.: +1-207-581-2156; Fax: +1-207-581-2202;
E-mail: Norton@Maine.edu

(dry deposition) (Iverfeldt, 1991), absorption of Hg^0 through leaf stomata (Frescholtz et al., 2003), and scavenging by wet precipitation and particulate matter. The global nature of Hg pollution since the onset of industrialization, and its enhanced biological availability, has driven research aimed at determining current and past Hg deposition rates using ice cores, peat bogs, and lake sediments as archives of atmospheric deposition. Deposition of Hg has increased substantially over the last 150 years as indicated in snow samples and marine sediment from Greenland (Boutron et al., 1998; Asmund and Nielson, 2000), Arctic Sea sediments (Gobeil et al., 1999), and ice cores from Wyoming, U.S. (Schuster et al., 2002). Peat cores from North America (Shotyk et al., 2004; Norton et al., 1997), the Faroe Islands (Shotyk et al., 2004), Sweden (Bindler, 2003), and Switzerland (Roos-Barracough et al., 2002) all indicate elevated atmospheric contributions of Hg. Lake sediments from Canada (Lucotte et al., 1995; Lockhart et al., 1998; Trip and Allan, 2000), the North American Arctic (Hermanson, 1998; Landers et al., 1998; Bindler et al., 2001a), the United States (Swain et al., 1992; Engstrom and Swain, 1997; Norton et al., 1997, 2004) and Sweden (Bindler et al., 2001b) show grossly similar trends in atmospheric Hg since the onset of industrialization. Many of these Hg archives occur in relatively remote regions with no known local anthropogenic point sources, thus pointing to the importance of atmospheric transport in the global cycling of Hg. Biester et al. (2002) suggested the possibility of inter-hemispheric Hg transport based on the accelerated Hg deposition rates recorded in a peat bog of the Magellanic Moorlands, Chile. Lamborg et al. (2002) quantified Hg deposition, utilizing peat and lake sediment cores from Nova Scotia, Maritime Canada, and New Zealand. The Nova Scotia results, along with results of other northeastern North American studies, serve as a regional comparison for the results presented here.

Mercury in the sedimentary environment has been quantified using a variety of analytical techniques and was historically reported as concentrations (e.g., ng Hg/g sediment). Concentrations were used to describe the movement of Hg within the environment, biomagnification within the food chain, and storage in lake sediments. Dry mass calculations for sediment (a function of the density of mineral and organic matter, water content, and

volume) can be coupled with concentration values for Hg, and the age of sediment in a core to determine Hg flux at the coring site, Hg mass/area-time. The use of fluxes overcomes some of the difficulties of interpreting pollution history using only changes in concentration. Engstrom and Wright (1984) stressed the importance of interpreting sediment records using fluxes to gain an accurate picture of the true deposition history.

Real-time data collection for monitoring and modeling fluxes of various Hg species to the Earth's surface has only become available recently (Pirrone et al., 1998; Munthe et al., 2001; Wängberg et al., 2001; NADP, 2004). These data are spatially restricted and cover, at best, only the last decade. Methods of inferring past deposition rates have been developed to compensate for direct measurements. Ombrotrophic peat provides the clearest record of atmospheric wet deposition of Hg to terrestrial systems (Shotyk et al., 2004; Norton et al., 1997; MacKenzie et al., 1998). Ombrotrophic bogs receive all nutrients from the atmosphere, minimizing the dilution of the atmospheric Hg source. Lake sediments also provide a continuous, long-term, reproducible record of atmospheric deposition through time, although their preserved record is complicated by the effects of in-lake and lake-watershed interactions caused by differences in lake basin geometry, sediment bioturbation and diagenesis, Hg point sources, and soil erosion. Additionally, the atmospheric deposition record in lake sediment is diluted by organic and inorganic detritus derived from shallower water, or from the watershed. Because lakes are more abundant and widely distributed than ombrotrophic bogs, lake sediment records are commonly used as proxies for atmospheric deposition of Hg to terrestrial environments. With increasing numbers of well-dated sediment records, there is a need for a consistent method of comparing values across widely spaced and highly variable lake environments.

A major focus of Hg studies is the comparison of atmospheric deposition before and after the onset of industrialization in a particular region. The onset of "significant" anthropogenic (industrial) atmospheric Hg contributions varies from location to location (Yang and Rose, 2003). Estimates of pre-industrial anthropogenic Hg contributions to the environment are site-specific and range widely, even for bog environments (Shotyk et al., 2004;

Martínez-Cortizas et al., 1999; Roos-Barraclough et al., 2002; Bindler, 2003). For lakes, these background values are unique to the study lake, and are determined by the physical, geologic, biological, and chemical characteristics of the lake and its watershed, and by the location of the lake with respect to atmospheric transport of naturally occurring Hg. In most temperate and boreal regions, natural atmospheric deposition (soil dust, volcanic and other gaseous emission sources), rather than local bedrock geology, is the most significant source of Hg in lake sediments, terrestrial soils, and terrestrial and aquatic biota (Meili, 1995). If estimates of background Hg deposition rates can be made, the relative impact of humans on Hg cycling can be assessed. Studies of long-term peat chemistry (Roos-Baraclough et al., 2002; Bindler, 2003) indicate that northern hemisphere atmospheric deposition of Hg was increased sensibly above background at least 500 years before present (BP) and has remained elevated since the onset of industrialization. However, only since about 1900 have anthropogenic contributions of atmospheric Hg increased dramatically (three to fivefold above background) in lake sediment records of the Upper Midwest U.S. (Swain et al., 1992), the northeastern USA. (Norton et al., 1997, 2004; Lorey and Driscoll, 1999; Perry et al., 2001; Kamman and Engstrom, 2002), and the Maritime Canada Provinces (Pilgrim et al., 2000; Lamborg et al., 2002). Three recent studies have examined the history of Hg pollution in lakes from the atmosphere in the northeastern USA (Lorey and Driscoll, 1999; Perry et al., 2001; Kamman and Engstrom, 2002). Results from these studies, plus unpublished data from Maine, have been merged into a single dataset to examine the spatial and temporal variability of the anthropogenic Hg flux to lake sediment. This study deconstructs the total Hg flux to these lake sediment archives to refine estimates of atmospheric inputs controlled by human activity. We develop a closer approximation of the true anthropogenic Hg flux across space and through time.

Methods and calculations

Lake selection

Most of the lakes are headwater lakes (Table 1). None of the lakes were under the influence of a

nearby surface point source of Hg. However, the cluster of eight lakes in central coastal Maine (Fig. 2) was investigated to determine if a local point source of atmospheric emissions (ca. 1000 kg/year in 1990, Maine Department Environmental Protection) for 37 years (1964–2001) caused excess atmospheric deposition of Hg in nearby lakes. There was no evidence linking sediment Hg accumulation rates to the local atmospheric emissions. Shoreline and watershed development for the entire lake set ranged from nearly pristine to urban. Details about the lakes and methods for the studies are in the original references (Table 1).

Coring and field processing

Sediment cores were retrieved from the deep portion of the lakes using a 4-inch acrylic-tube stationary piston corer (ME, NH, NY and VT) (Davis and Doyle, 1969) or a 6-cm diameter gravity corer (VT) (Table 1). Gravity corers may collect slightly less mass in longer cores (yielding lower accumulation rates) due to progressively increasing compression with depth (Cumming et al., 1993). This effect would be minimal in the upper 0–20 cm of sediment, the depth interval of interest in our lakes. Sediment was most commonly sectioned at the lake with stainless steel or plastic ware and placed directly into pre-labeled Whirlpack™ (or similar) bags. The core sectioning method generally consisted of 0.5, 1 and 2 cm intervals for depths to 10, 10–30 and > 30 cm, respectively, for ME lakes, and of 1 cm intervals throughout the core, for NH and VT cores. New York cores were sectioned at 0.5 cm intervals from 0 to 30 cm and at 1 cm intervals below 30 cm. Samples were stored in coolers until returned to the laboratory.

General laboratory procedures

Sample processing

Details for processing and analyses are presented in the original papers. Each sediment interval was manually homogenized in its sample bag until uniform (5–10 min). A series of wet aliquots were placed in large, acid-washed crucibles and dried at 35–40 °C except for Kamman and Engstrom (2002, 60 °C) for one to two weeks. Mercury volatilization is not appreciable up to and including

Table 1. Physical characteristics of lakes considered for the compilation

Name (State)	Longitude/ Latitude	Lake area, ha	Watershed area, ha ^a	Maximum depth, m	References
Bear (NY)	74°17'12"/44°23'45"	21.9	63.7	18.3	Lorey and Driscoll (1999)
Big Moose (NY)	74°51'53"/43°49'02"	504	9051	22.3	Lorey and Driscoll (1999)
Bourn (VT)	73°00'16"/43°06'19"	13.8	117.5	8.5	Kamman (2003)
Branch (VT)	73°01'10"/43°04'56"	19.4	188.6	10.7	Kamman (2003)
Brewer (ME)	68°43'35"/44°42'40"	356.4	3107.9	15	This paper
Carmi (VT)	44°58'20"/72°52'35"	567.4	3120.2	10	Kamman and Engstrom (2002)
Clear (NY)	73°49'50"/43°59'50"	70.4	530.2	24.4	Lorey and Driscoll (1999)
Cliff (ME)	69°15'00"/46°23'46"	228	2436	19.8	This paper
Dudley (NH)	71°50'30"/43°07'30"	12.1	673.4	6.1	Kamman and Engstrom (2002)
Gilman (NH)	71°12'00"/43°30'30"	13	255.4	5.2	Kamman and Engstrom (2002)
Goose (ME)	68°34'32"/44°39'40"	81.7	852.11	10	This paper
Grout (VT)	72°56'34"/42°02'34"	34.0	150.6	9	Kamman (2003)
High (VT)	73°09'14"/43°45'10"	8.1	70	16	Kamman and Engstrom (2002)
Hodgdon (ME)	68°23'49"/44°19'22"	14	~140	6.7	This paper
Intervale (NH)	71°31'30"/43°47'30"	17.4	466.2	14.9	Kamman and Engstrom (2002)
Jacob Buck (ME)	68°44'39"/44°38'46"	76.9	663	16	This paper
Little Echo (NY)	74°21'25"/44°18'20"	1	0	4.9	Lorey and Driscoll (1999)
Klondike (ME)	68°56'56"/45°55'40"	2	Unknown	2.7	This paper
Long (ME)	68°40'59"/44°39'26"	89.8	5827.4	9	This paper
Lobster (ME)	69°31'04"/45°51'49"	1406	9152	32.6	This paper
McConnell (VT)	71°48'06"/44°49'04"	35.2	1465.4	5.5	Kamman and Engstrom (2002)
Merriam (NY)	74°50'45"/43°51'22"	8.1	234.8	5.2	Lorey and Driscoll (1999)
Queer (NY)	74°48'25"/43°51'22"	54.5	100.1	21.3	Lorey and Driscoll (1999)
Ragged (ME)	69°22'50"/45°49'32"	1098	10300	16.5	This paper
Seboeis (ME)	68°53'12"/45°53'12"	1700	15254	21.3	This paper
Sessions (NH)	71°11'50"/44°42'20"	14.2	207.2	10.3	Kamman and Engstrom (2002)
Spring (VT)	72°55'12"/43°29'42"	26.7	111.3	24	Kamman and Engstrom (2002)
Stratton (NH)	72°58'10"/43°06'17"	18.6	107.6	5	Kamman (2003)
Swetts (ME)	68°46'50"/44°41'59"	50.6	883.2	8	This paper
Thurston (ME)	68°43'33"/44°39'50"	57	637.1	7.6	This paper
Trout (ME)	68°44'56"/44°40'01"	4.9	69.9	> 7	This paper
U. Wallface (NY)	74°03'15"/44°08'47"	5.5	52.8	11.9	Lorey and Driscoll (1999)
Wallingford (VT)	72°54'32"/43°23'41"	35.2	594.9	7	Kamman and Engstrom (2002)
West (NY)	74°03'15"/43°48'41"	10.4	97.7	5.2	Lorey and Driscoll (1999)
Wheeler (VT)	71°38'29"/44°42'30"	26.7	1683.1	10	Kamman and Engstrom (2002)
Willard (NH)	72°01'30"/43°01'30"	38.9	414.4	17.7	Kamman and Engstrom (2002)
Williams (ME)	68°46'20"/44°39'33"	45.3	453.3	16	This paper

^aWatershed area does not include lake surface area.

temperatures of 60 °C, based on results of experiments conducted prior to processing all samples. Typically, ceramic crucibles and other implements were washed with deionized water, soaked for a minimum of 24 h in 10% hydrochloric acid (HCl), rinsed four times with tap and deionized water, and air dried. The remainder of the sediment was transferred to a large acid-washed crucible and dried at 90–110 °C to constant weight.

Homogenization and archiving

The dried sediment (40–60, or 90–110 °C) from a core was pulverized and homogenized using a

mortar and pestle. The sediment was transferred to cleaned glass vials for long-term archiving. All glass storage vials, and the mortar and pestle, were soaked in 10% HCl for 24 h, rinsed four times with tap and deionized water, and air-dried, prior to use. They were not re-cleaned between samples.

Sample H₂O, Loss-on-ignition, and digestion

The intervals of sediment dried at ca. 100 °C were used to calculate percent water and for radiometric dating (²¹⁰Pb). A 0.3–0.5 g aliquot was transferred to an acid washed crucible, warmed to 550 °C, and ashed at 550 °C for 3 h. Dry (ca. 100 °C) and

ashed weights were used to calculate loss-on-ignition (LOI) for each interval. The LOI is assumed to be oxidizable organic materials, although dehydration of metal hydroxides, especially of Al and Fe, contributes to the weight loss.

Mercury analysis preparation

Sediment from cores retrieved in the early 1980s (Norton et al., 1992) was not analyzed for Hg until 1998 (Lorey and Driscoll, 1999). Intervals dried at 40–60 °C were used for total Hg. About 0.4–0.5 g of each interval was digested using a microwave-assisted acid digestion technique. Mercury was brought into solution through leaching with some combination of nitric and hydrochloric acids, or sulfuric acid, and closed vessel heating by microwave, followed by oxidation with permanganate/persulfate solutions. Hydroxylamine hydrochloride was added to the digestate and then brought to 100 ml with deionized water. Solutions were filtered and stored until analysis.

Mercury analyses

Concentrations of Hg were determined by cold vapor (flameless) atomic absorption spectrophotometry using a flow injection Hg system (FIMS). Precision and accuracy were typically checked by analysis of standard reference materials (SRM), blanks, duplicate analyses, replicate digestions, and periodic check standards during a run. Typically, one SRM and one replicate were digested per 10 samples, and a blank was prepared every 10 samples. One check standard was run for every 10 analyses.

Radiometric dating

The cores retrieved in the early 1980s and reported by Lorey and Driscoll (1999) were dated by alpha analysis for ^{210}Pb (Eakins and Morrison, 1978) at the University of Maine (Norton et al., 1992). The cores in Kamman and Engstrom (2002) were retrieved in 1998 and dated by the same general technique. For the cores retrieved in the 1990s in Maine, ^{210}Pb gamma-ray activity was determined using the 46.52 keV emission peak. A Canberra germanium well detector (1 by 4 cm) with 22.5% efficiency for ^{60}Co was utilized. Dried sediment in capped 1 by 4 cm polyethylene vials was equilibrated for at least three weeks, and then counted for 43,200–259,200 s. Data were analyzed by Compton

continuum subtraction of the peaks and processed using *GammaTrac* software (Oxford Instruments). The detector was calibrated using U.S. EPA National Exposure Research Laboratory aqueous standards (^{210}Pb , ^{241}Am , ^{226}Ra , ^{137}Cs , and ^{60}Co) in the same geometry as the sediment samples. The unsupported ^{210}Pb activity ($^{210}\text{Pb}_u$) for all cores was estimated by subtracting the constant background ^{210}Pb activity ($^{210}\text{Pb}_b$), deep in the core, from total ^{210}Pb ($^{210}\text{Pb}_t$). The integrated $^{210}\text{Pb}_u$ ($\Sigma^{210}\text{Pb}_u$) (Bq $^{210}\text{Pb}_u/\text{cm}^2/\text{core}$) is necessary for dating and assessing the sediment-focusing factor. Calculation of interval mid-point ages for all cores was based on the Constant Rate of Supply (CRS) model of Appleby and Oldfield (1978). Linear interpolation between interval mid-point ages was used to calculate ages of interval boundaries, permitting the calculation of deposition rates of sediment, total Hg, and anthropogenic Hg.

Anthropogenic Hg deposition calculations

Algorithms have been developed to assess better the magnitude of anthropogenic Hg contributions to lake sediment. The calculation sequence involves the determination of sediment accumulation rates, total, variable and atmospheric Hg deposition rates, and finally, normalization for sediment focusing.

Data requirements and calculations for the sediment accumulation rates include:

- Interval thickness (e.g., 0.0–1.0 cm)
- Water concentration in interval (% H_2O)
- Loss-on-ignition (LOI) – typically interpreted as the % oxidizable organic matter, but including any loss of water of hydration (e.g., from dehydration of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$)
- Concentration of Hg (ng Hg/g dry sediment)
- Total, unsupported, and supported ^{210}Pb in intervals, integrated $\Sigma^{210}\text{Pb}_u$ (Bq/ cm^2)
- Age of midpoints of intervals, corresponding to concentration data for entire intervals (years)
- Age of boundaries of intervals (years)
- Years per interval

The accumulation rate for Hg in an interval of sediment is:

$$\begin{aligned} & [(g \text{ of sediment/interval-cm}^2) \\ & \times (\text{concentration of Hg in interval})] \\ & = (g \text{ of Hg/interval-cm}^2) \end{aligned} \quad (1)$$

$(g \text{ of Hg/interval-cm}^2)/(\text{years represented by interval}) = \text{accumulation rate (g Hg/cm}^2 \text{ year)}$ (2)

The dry mass/cm² (DM), g/cm², for all cores is given by

$$DM = [PS * (100 - VW) * Z]/100 \quad (3)$$

where Z = thickness of interval (cm) and

$$VW = \text{volume \% of water in } 1 \text{ cm}^3 = \{(\% \text{ H}_2\text{O}) / (\% \text{ H}_2\text{O} + [100 - \% \text{H}_2\text{O}]/PS)\} * 100 \quad (4)$$

where

$$\begin{aligned} PS &= \text{solid density, g/cm}^3 = [(\rho_o) \\ & \times (\% \text{ organic matter, dry weight basis}) \\ & + (\rho_i)(\% \text{ inorganic matter})]/100, \end{aligned} \quad (5)$$

where ρ_o is the density of organic matter and is assigned the value 1.6, ρ_i is the density of inorganic matter and is assigned the value of 2.5, and % inorganic matter = (100% - % organic matter). This calculation from %H₂O and LOI can be avoided if very accurate volumetric samples are taken during core sectioning, dried, and mass/volume is determined for the dry matter. However, the errors for small volumetric samples may be appreciable.

The net accumulation rate for total Hg ($\mu\text{g Hg}_T/\text{m}^2 \text{ year}$) is given by:

$$\begin{aligned} \text{Hg}_T &= [(\text{mass of sediment/interval/cm}^2) \\ & (\text{concentration of Hg in interval})]/(\text{years/interval}) \end{aligned} \quad (6-1)$$

This total Hg flux is composed of three components.

$$\text{Hg}_T = \text{Hg}_B + \text{Hg}_V + \text{Hg}_A \quad (6-2)$$

1. The natural background flux of Hg (Hg_B) represents the ambient levels of Hg introduced to

the sediment as a function of local geology and atmospheric transport from natural sources such as volcanoes, the marine surface, and soil dust. Commonly, variations in % organic matter relate to variations in Hg concentration measured in sediments (Lucotte et al., 1995). Instability in background flux of Hg is likely caused mostly by variable flux of Hg associated with particulate organic matter.

2. Variations in the gross sedimentation rate caused by human activities or natural disturbances in the watershed cause variations in the sedimentation rate of Hg (Hg_V). Hg_V is estimated as follows:

$$\begin{aligned} \text{Hg}_V &= [(\text{sedimentation rate for any sediment} \\ & \text{interval}\{g/\text{cm}^2 \text{ year}\})/(\text{pre-1875 sedimentation} \\ & \text{rate}\{g/\text{cm}^2 \text{ year}\})] * \text{Hg}_B - \text{Hg}_B. \end{aligned} \quad (6-3)$$

If the pre-1875 sedimentation rate equals the post-1875 sedimentation rate, the ratio = 1, and only the value of Hg_B is subtracted from Hg_T in Equation (6-2). A ratio value >1 indicates that the post-1875 sediment accumulation rate exceeds the pre-1875 rate, a common occurrence. For example, if the ratio = 2, $\text{Hg}_V = \text{Hg}_B$, and a value equal to $2 * \text{Hg}_B$ is subtracted from the Hg_T value in Equation (6-2).

3. Deposition of anthropogenic Hg (Hg_A) directly to the lake (atmospheric, on-lake point source, or surface water) and leaching of Hg from the watershed to the lake may occur. In locations where there is no known point-source or bedrock source of Hg, Hg_A is interpreted to represent the atmospheric signal of anthropogenic Hg in the lake sediment.

Redistribution of sediment within a lake basin is strongly influenced by the general geometry of the basin. The Hg_A value is corrected further for the effects of lake basin geometry and focusing (yielding $\text{Hg}_{A,F}$; see below). The basis of the focusing correction is the ratio of the lake-specific $\Sigma^{210}\text{Pb}_u$ ($\Sigma^{210}\text{Pb}_{u, \text{local}}$) to the regional value ($\Sigma^{210}\text{Pb}_{u, \text{regional}}$). $\Sigma^{210}\text{Pb}_u$ in Maine ombrotrophic bogs has been estimated at 0.444 Bq/cm². The focusing factor (F) is calculated as (Table 2):

Table 2. Focusing factors for each sediment core used in the final database

Lake	$\Sigma^{210}\text{Pb}_u$ (Bq/cm ²)	Focusing factor
Bear, NY	0.16	0.37
Beaver, NH	0.68	1.55
Big Moose, NY	0.65	1.47
Branch, VT	0.47	1.08
Brewer, ME	0.72	1.63
Carmi, VT	0.67	1.52
Clear, NY	0.57	1.29
Cliff, ME	0.80	1.80
Dudley, NH	0.41	0.93
Gilman, NH	0.25	0.57
Goose, ME	0.83	1.88
High, VT	0.54	1.24
Intervale, NH	0.46	1.05
Jacob Buck, ME	0.88	1.98
Little Echo, NY	0.07	0.16
Long, ME	0.60	1.35
McConnell, VT	0.42	0.95
Merriam, NY	0.28	0.64
Queer, NY	0.62	1.41
Sessions, NH	0.39	0.89
Spring, VT	0.81	1.85
Swetts, ME	0.70	1.59
Thurston, ME	0.60	1.36
Trout, ME	0.21	0.47
U. Wallface, NY	0.24	0.54
Wallingford, VT	0.46	1.04
West, NY	0.29	0.66
Wheeler, VT	0.39	0.87
Willard, NH	0.47	1.06
Williams, ME	1.23	2.77

$$F = (\Sigma^{210}\text{Pb}_{u,\text{local}})/(\Sigma^{210}\text{Pb}_{u,\text{regional}}) \\ = (\Sigma^{210}\text{Pb}_{u,\text{local}})/0.444\text{Bq/cm}^2 \quad (7)$$

The value of $\Sigma^{210}\text{Pb}_{u,\text{regional}}$ is likely linearly proportional to total wet precipitation (Appleby, pers. comm.). Lacking precipitation data for each site, we assumed a constant regional value. Variation of precipitation over the region is from about 1 to 1.5 m/year (NADP, 2004). A focusing factor value greater than 1 implies the presence of more $^{210}\text{Pb}_u$ winnowed from shallower portions of the lake basin than would be expected if no redistribution of sediment or $^{210}\text{Pb}_u$ occurred. Sediment that is winnowed into the deeper portion of the lake also carries Hg, thus increasing the Hg accumulation rate. Dividing the Hg_A value for each lake by the appropriate focusing factor yields a

refined assessment of anthropogenic Hg deposition to the lake sediment. The final algorithm that was applied to the northeastern USA sediment core database was:

$$\text{Hg}_{A,F}(\mu\text{g Hg/cm}^2 - \text{year}) = [\text{Hg}_T - \text{Hg}_B - \text{Hg}_V]/F \quad (8)$$

Where LOI and H_2O concentrations are relatively constant in a core, we used linear interpolation to determine missing deposition and sediment interval age values. Some surface sediment had irregular chemistry, possibly due to sediment resuspension by gas evolution during coring, followed by incomplete settling, or to diagenetic processes. These values have been used unaltered and they translate through to the accumulation rate calculation. Sharp peaks in the deposition rate profiles are commonly due either to counting errors associated with very low concentrations of ^{210}Pb in older sediment (most cases), or to heterogeneous surface sediment chemistry. Unusual ^{210}Pb counts cause perturbations in the accumulation rates for several adjacent intervals of sediment but do not obfuscate the general trends. Values for $\text{Hg}_{A,F}$ at 1850, 1900, 1950, 1975 and 1990 were calculated by linear interpolation of the $\text{Hg}_{A,F}$ versus ^{210}Pb date relationships.

Results and discussion

The results of deconvolution of the sediment record are shown in detail for Jacob Buck Pond, Maine, USA, one of the lakes in the regional synthesis (Fig. 1). The concentration of Hg ranged from 100 ng Hg/g dry sediment in 1875 to 250 ng/g at the end of the 20th century. Ignoring accumulation rates, it is tempting to say that Hg accumulation has increased by 150%. However, the total accumulation rate (Hg_T) ranged from 20 to 170 $\mu\text{g/m}^2$ year, an increase of 750%. For this lake, the average background value (pre-1875) for the total Hg flux (Hg_B) is estimated at 20 $\mu\text{g/m}^2$ year. If that value is subtracted from Hg_T and the variable sediment accumulation rate is factored in, then Hg_A ranges from 0 (1875) to about 150 $\mu\text{g/m}^2$ year. The apparent absolute increase of Hg has been reduced by nearly 50%. Finally, if focusing is normalized, the $\text{Hg}_{A,F}$ accumulation

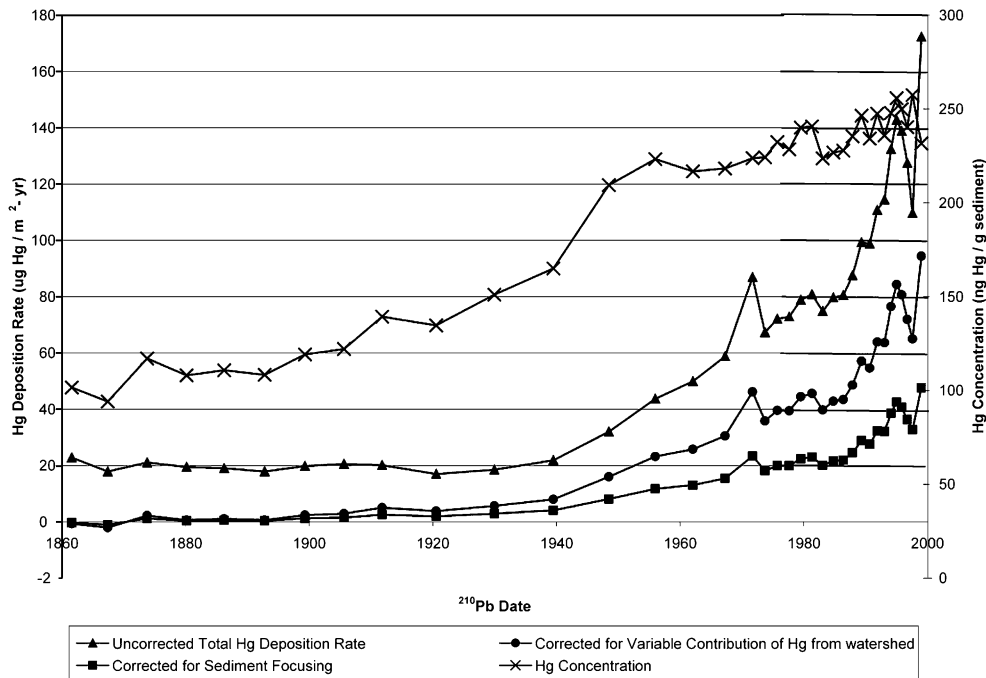


Figure 1. Mercury concentration and the deconvolution of total Hg deposition rates to yield an estimation of anthropogenic Hg deposition rates in sediment at Jacob Buck Pond, Maine, USA.

rate increases from 0 to $50 \mu\text{g}/\text{m}^2 \text{ year}$. It is $\text{Hg}_{\text{A,F}}$ that is compared from site to site. Sediment cores from the Maine, New Hampshire/Vermont, and the Adirondack region of New York, datasets, were first evaluated on the basis of whether background values for ^{210}Pb activity, Hg_{T} deposition rate, and sediment deposition rate were reached and were stable (Table 3). Most sediment cores used in this compilation had a sediment record that extended back to supported $^{210}\text{Pb}_{\text{b}}$ values. Lakes with background (pre-1875) instability of either (or both) sediment deposition rate and Hg_{T} deposition rate profiles prevented determination of Hg_{A} deposition rates through time. Although these lakes still provide useful general Hg accumulation rate trends, Hodgdon, Klondike, Mud, Speck and Spring were excluded from the deconstruction calculations because of instability in background sediment deposition rates or in Hg_{T} deposition rates that produced negative Hg_{A} deposition values in recent sediment. Deconstruction of the Hg_{T} flux to the sediment enables lakes with different physical parameters to be compared in terms of Hg_{A} contribution. Sediment records of Hg_{T} accumulation in lakes across the northeastern

USA, after the application of corrections for in-watershed and in-lake processes, show a similar history of Hg_{A} contribution through time. This history is characterized by an initial increase of Hg_{A} deposition rates around the turn of the century, with maximum values reached between 1975 and 1990.

Time slices taken across the region compare the spatial distribution of Hg deposition values at a specific ^{210}Pb date (Fig. 2). No lakes in this dataset show a decrease in focusing-corrected Hg_{A} deposition rates from 1970 to 1980. While some of the lakes show modest decreases in Hg_{T} on the basis of the most recently retrieved sediment cores (1990s), our estimates of $\text{Hg}_{\text{A,F}}$ show only a leveling off or slight decrease in accumulation rates (Fig. 2). Several lines of independent evidence (peat and lake sediment cores, Norton et al., 1997, 2004; forest soils, Evans et al., in review) suggest that Hg_{A} deposition has declined more than 50% since 1970. The lack of response of many lake sediment records to the decline may be attributed to the high retention of Hg within watershed soils and biomass, and to the subsequent leakage of Hg from the watershed, even as the atmospheric

Table 3. Data resolution for all cores considered for the compilation

Lake (State)	²¹⁰ Pb		Sectioning resolution ^a		Sediment deposition rate		Hg values	
	Background reached	Number of data points (post-1900)	0.5 cm	1 cm	Background stable?	Number of data points (post-1900)	Background stable?	Number of data points (post-1900)
Bear (NY)	Y	20	×		Y	20	Y	14
Beaver (NH)	N	9		×	N	9	N	12
Big Moose (NY)	Y	33	×		Y	33	Y	29
Bourn (VT)	Y	14		×	Y	14	Y	13
Branch (VT)	Y	9		×	N	9	N	12
Brewer (ME)	Y	10	×		Y	10	Y	33
Carmi (VT)	Y	6		×	Y	6	Y	12
Clear (NY)	Y	18	×		N	18	N	9
Cliff (ME)	Y	9	×		Y	9	Y	32
Dudley (NH)	Y	8		×	Y	8	Y	9
Gilman (NH)	Y	8		×	Y	8	Y	10
Goose (ME)	Y	9	×		Y	9	Y	29
Grout (VT)	Y	10		×	N	10	Y	8
High (VT)	Y	5		×	Y	5	Y	9
Intervale (NH)	Y	8		×	Y	8	Y	9
Jacob Buck (ME)	Y	9	×		Y	9	Y	29
Klondike (ME)	Y	12	×		N	12	N	12
Little Echo (NY)	Y	17	×		N	17	N	8
Long (ME)	Y	11	×		Y	11	Y	41
Lobster (ME)	Y	10		×	Y	10	Y	23
McConnell (VT)	Y	7		×	Y	7	Y	13
Merriam (NY)	Y	13	×		Y	13	Y	11
Mud (ME)	Y	5	×		N	5	N	5
Queer (NY)	Y	36	×		Y	36	Y	30
Ragged (ME)	Y	8		×	Y	8	Y	10
Seboeis (ME)	Y	11		×	Y	11	Y	19
Sessions (NH)	Y	7		×	N	7	Y	11
Speck (ME)	Y	9	×		N	9	N	9
Spring (VT)	Y	7		×	N	7	Y	13
Stratton (NH)	Y	10		×	Y	10	Y	13
Swetts (ME)	Y	16	×		Y	16	Y	25
Thurston (ME)	Y	12	×		N	12	Y	37
Trout (ME)	Y	9	×		Y	9	Y	31
U. Wallface (NY)	Y	16	×		Y	16	Y	11
Wallingford (VT)	Y	5		×	Y	5	Y	11
West (NY)	Y	19	×		N	19	Y	11
Wheeler (VT)	Y	5		×	Y	5	Y	10
Willard (NH)	Y	9		×	Y	9	Y	10
Williams (ME)	Y	12	×		Y	12	Y	30

^aIn the upper core.

contribution is reduced. The role of watershed size and dissolved organic carbon transport as controlling factors is discussed in Kamman and Engstrom (2002), Kamman (2003), Lorey and Driscoll (1999) and Dennis et al. (2005). The linkage between watersheds and the Hg profile recorded within that lake's sediments speaks to the importance of accurately classifying the physical char-

acter of the watersheds in any study (land use, percentage of wetland). As interpreted using Hg_T, lakes in areas strongly influenced by proximal Hg sources show a recent decline in atmospheric Hg contributions (Engstrom and Swain, 1997), as do kettle lakes where transport of particulate Hg from the catchment is very low (Norton et al., 2004), and some remote Vermont and New Hampshire

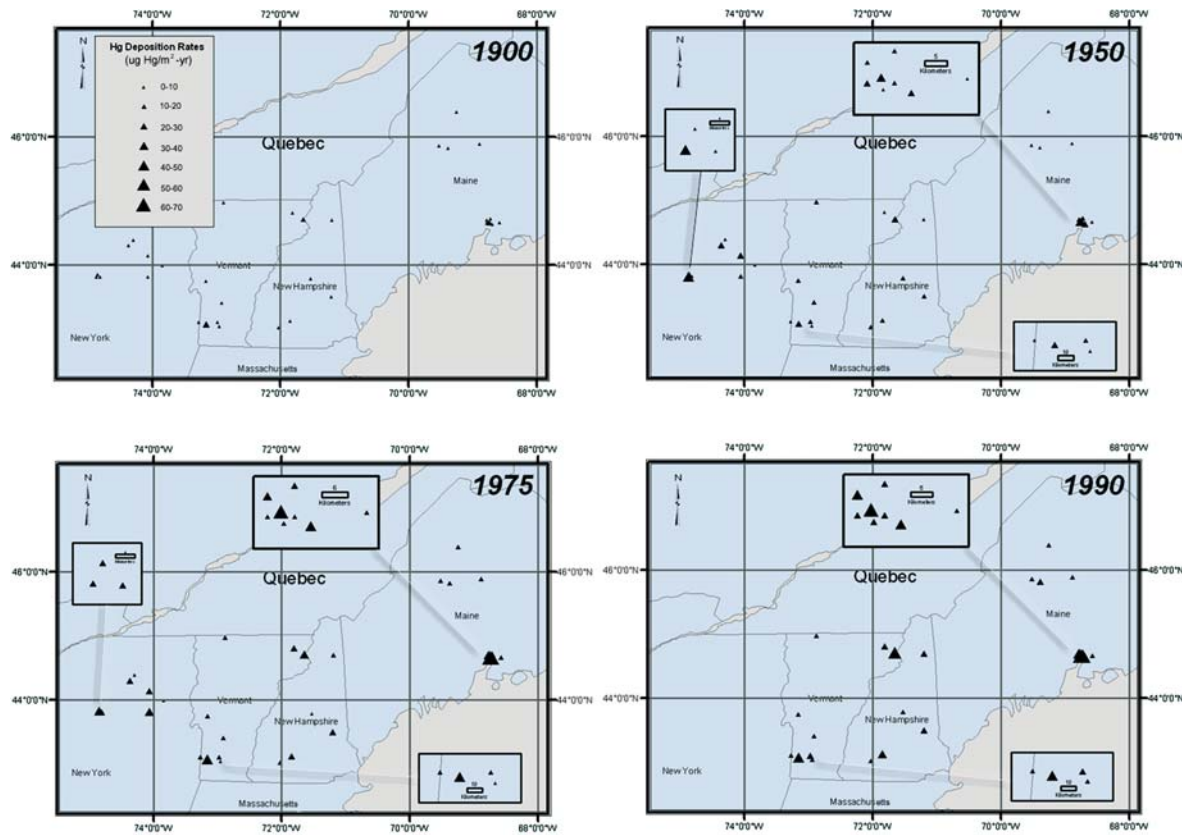


Figure 2. Anthropogenic Hg deposition rates across time and space. New York data for 1990 were unavailable.

lakes (Kamman and Engstrom, 2003). The average northeastern USA total Hg burden in wet precipitation for 1998 was $7.9 \mu\text{g Hg}/\text{m}^2 \text{ year}$ (NADP, 2004). Although the extrapolation of lake-core records to substantially larger areas is not legitimate, average calculated Hg_T values equal $41 \mu\text{g Hg}/\text{m}^2 \text{ year}$, about 400% more than wet deposition. However, many recent studies indicate that dry deposition typically exceeds wet deposition, commonly by a factor of 2 to 3. Thus, the lake sediment $\text{Hg}_{A,F}$ accumulation rates, adjusted as described above, may provide a reasonable proxy for total atmospheric deposition magnitude and trends for forested ecosystems.

Normalization for sediment focusing

We assumed that sediment cores represent continuously deposited, undisturbed sediment, and that the Hg record in the sediments is proportional to the total Hg load deposited to a lake. Any

within-lake processes that affect the mobility of Hg will complicate interpretation of sediment cores as a proxy for the atmospheric record (Lockhart et al., 2000). Gobeil et al. (1999) reported that remobilization and diffusion of Hg within lake sediment can occur under conditions of very low sedimentation rates and/or oxidation. If the sediment were anoxic, as is typical only a few cm below the sediment–water interface, diffusion and biologically-induced migration of Hg within the sediment column would likely be greatly diminished.

Several key assumptions were made in the derivation of corrected anthropogenic Hg deposition maps:

1. The background Hg deposition rates (Hg_B) and sediment deposition rate values (pre-1875 value) are representative for the lake and watershed processes prior to major human

influence. Several studies have demonstrated that the determination of background values of atmospheric pollutants is difficult. For example, Hg deposition under non-pollution conditions in peatlands may vary by over an order of magnitude, likely as a consequence of variable vegetation, microtopography, and the associated variation in dry deposition capture (Norton et al., 1997; Martínez-Cortizas et al., 1998; Roos-Barraclough et al., 2002; Bindler, 2003). These background values are a reference point for the individual lake, enabling the regional comparison of lakes. Calculating the ratio of background Hg accumulation rates to values measured in more recent sediment eliminates watershed-specific processes from the determination of $Hg_{A,F}$.

2. A large fraction of Hg in surface water is transported in particulate form. Ten to 20% is typically associated with dissolved organic carbon during transport from watersheds to lakes (Swain et al., 1992; Lucotte et al., 1995; Grigal, 2002; Shanley et al., 2002a, b). The proportion of pre-pollution to pollution Hg in the recent flux is generally unknown. In our calculations we assume that all the Hg mobilized from the watershed and incorporated into the lake sediment record is pre-pollution Hg. Thus, Hg_V is assumed to not contain pollution-related Hg. The concentration of Hg in the Hg_V flux is the same as in Hg_B . The actual Hg_V contribution is likely to be underestimated, because the terrestrial soils that are redistributed into the lake likely contain pre-1875 Hg and Hg_A . It may be possible to utilize Hg concentration trends in watershed soil profiles to better assess the time-varying contribution of Hg, and to provide a better estimate for the highly significant Hg_V term. Underestimation of Hg_V causes overestimation of Hg_A and shifts anthropogenic contributions forward in time because of the lag between deposition on the landscape, erosion of this Hg, and deposition at the coring site.
3. Sediment focusing of Hg and ^{210}Pb is assumed to be a non-episodic, linear redistribution mechanism that has operated during the time represented by the sediment core. The calculation of a focusing factor involves integrating $^{210}Pb_u$ activity within the sediment section and

comparing this value to the average cumulative flux of $^{210}Pb_u$ to the region, as inferred from studies of ombrotrophic peat, an archive in which Pb is immobile (Shotyk et al., 2004). In effect, this correction converts each lake basin to one of standardized geometry, where the basin is flat and sediment focusing does not occur. This normalization allows for the direct comparison of lakes within the same region, regardless of differences in lake-basin geometry. In theory, some $^{210}Pb_u$ is eroded from the landscape and deposited at the coring site, increasing the focusing factor (Equation 7). If this process is steady state, averaged over years, ^{210}Pb dating is possible. If not, then the CRS model is somewhat compromised.

The normalization transforms data so that lakes of widely varying physical character, but which are located within a region affected by similar atmospheric processes (and consequently, atmospheric contaminant transport), can be compared and can contribute to a synoptic temporal and spatial picture of atmospheric pollution (Figs 2 and 3). The range of variability in corrected, focus-adjusted Hg_A deposition rates is substantially reduced over that of the unmodified data. However, closely spaced lakes (clusters, see insets in Fig. 2) are highly variable and differences among lakes within a cluster are persistent through time. Using our assumption that Hg_V contains only pre-pollution Hg, the anthropogenic contribution (Hg_A) is substantially less (commonly <50%) than the Hg_T . However, the general trend of the data (increasing Hg deposition from 1900 to ca. 1980–1990) does not change significantly between the corrected and uncorrected data. For example, the uncorrected mean Hg_T for 1950 is $41 \mu\text{g}/\text{m}^2$ year, whereas the mean $Hg_{A,F}$ is $17 \mu\text{g}/\text{m}^2$ year (Fig. 3). Our calculations clearly indicate that if the Hg_T deposition rate were inferred to represent solely anthropogenic influences, then the human impact would be significantly overestimated. The corrections result in a clearer picture of the regional and temporal nature of Hg deposition patterns by reducing the strong influence of physical heterogeneities among lake systems (Fig. 2). Our deconstruction algorithms improve the accuracy of $Hg_{A,F}$ estimates and reinforce the inferences of numerous researchers, based on Hg_T trends.

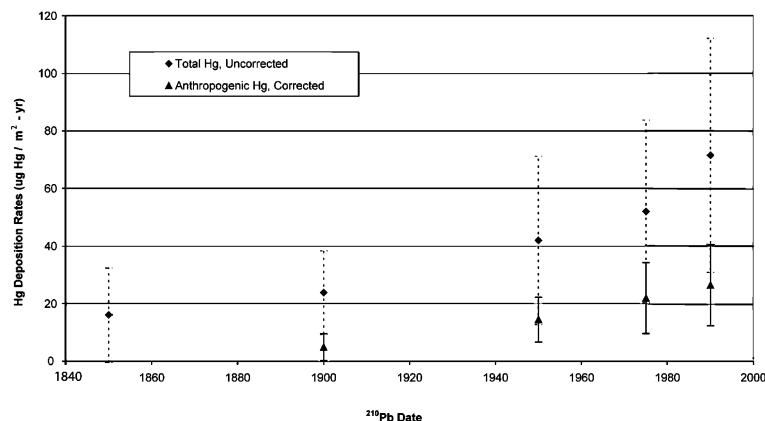


Figure 3. Focusing-corrected anthropogenic Hg deposition rates (Hg_A) compared to total Hg deposition rates (Hg_T) for all lakes. Error bars represent one standard deviation.

Trends exhibited by most lakes in this dataset indicate that the Hg deposition pattern couples regional depositional fields through time with the interactions among watershed processes and Hg storage and transport within lake systems. Many lake-watershed interactions (Dennis et al., 2005; Shanley et al., 2005) are complex, and difficult to assess and model effectively.

The cluster of eight lakes near Orrington, Maine (Fig. 2, inset) illustrates several important points of the normalization procedure. First, the anthropogenic component of the sediment Hg flux is much less than the total (e.g., Jacob Buck Pond, Figs 1 and 4). A substantial response in sediment Hg accumulation rates corresponding to reduced atmospheric deposition of Hg is an unrealistic expectation (see also Kamman and Engstrom, 2002). Second, temporal coherence between the local (Orrington, Maine, Fig. 4) and regional trends (Fig. 2) are apparent, suggesting little or no influence by local point source atmospheric emissions of Hg. Third, even on a local scale (eight lakes within a 10 km radius), $Hg_{A,F}$ accumulation rates differ significantly, implying significant watershed and lake controls on the Hg_A flux to individual lakes and variable sedimentation at the coring sites.

Geographically pertinent comparisons

Other studies have utilized lake sediment cores to assess atmospheric Hg deposition in the upper mid-western (Swain et al., 1992) and northeastern

USA, and in eastern Quebec (Landers et al., 1998) and Maritime Canada (Lamborg et al., 2002). Because Hg has a long atmospheric residence time, the Hg deposition signal identified at any single lake may be strongly influenced by regional processes, as well as localized processes. These studies from these broadly distributed regions can be compared to assess the assumptions used in the watershed-lake interaction model. Swain et al. (1992) corrected for watershed area/lake area and determined that the mean maximum atmospheric Hg deposition rate for mid-continental North America was $12.5 \mu\text{g}/\text{m}^2 \text{ year}$. Landers et al. (1998) compiled lake sediment data from the arctic and sub-arctic, including a suite of six eastern Quebec lakes. These Quebec lakes yielded background Hg deposition (our Hg_B) estimates of $2.6\text{--}24.1 \mu\text{g}/\text{m}^2 \text{ year}$, and maximum total Hg deposition (Hg_T) estimates ranging from 5.3 to $51.6 \mu\text{g}/\text{m}^2 \text{ year}$. This yields estimates for atmospheric Hg deposition ranging from 4 to $27 \mu\text{g}/\text{m}^2 \text{ year}$. Lamborg et al. (2002) incorporated a sediment focusing factor correction and estimated the maximum corrected atmospheric Hg flux to range from 5 to $20 \mu\text{g}/\text{m}^2 \text{ year}$ for three Nova Scotian lakes. Our study estimates Hg_A deposition to range from about 10 to $60 \mu\text{g}/\text{m}^2 \text{ year}$, with maximum values generally being reached between 1970 and 1990, and averaging $25 \mu\text{g}/\text{m}^2 \text{ year}$. There is general coherence among these estimates. Our average Hg_A is near the upper estimates for the other cited studies.

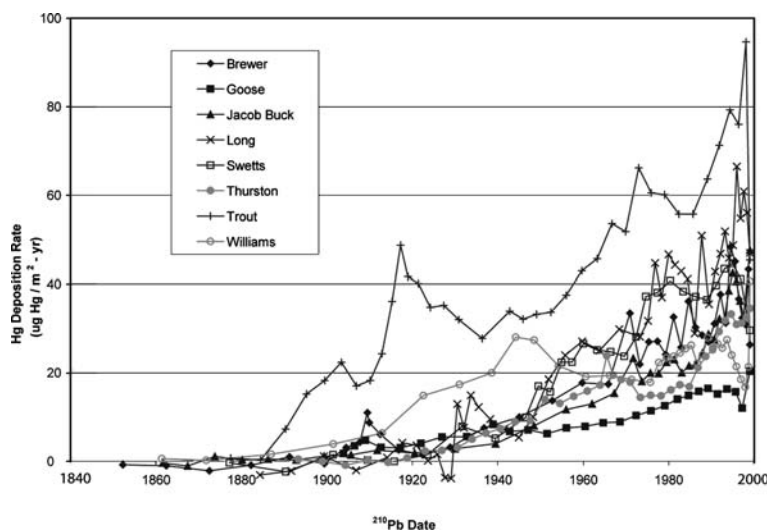


Figure 4. Corrected anthropogenic Hg deposition rates ($Hg_{A,F}$) in a cluster of eight Maine lakes, central Maine, USA.

The time represented by these cores does not overlap with the wet deposition rates measured by the NADP (2004) Hg network in the USA. If data from 1999 to 2003 are spatially consistent with earlier times, then the variability among closely-spaced lakes (Orrington, Maine cluster, Fig. 4) and among regions (Fig. 2) is more likely caused by post-atmospheric deposition processes.

Conclusions

Lake sediments represent a chemically stable and well distributed proxy for historic and pre-historic atmospheric deposition rates of Hg. The Hg deposition values to lake sediments has been deconstructed by assessing background deposition of Hg, variability of sediment accumulation rate, and sediment focusing so as to determine past atmospheric contributions caused by human activity. Maximum total Hg accumulation rates over the 20th century in the lake set from the northeastern USA ranged from 27.1 to 175.4 $\mu\text{g Hg}/\text{m}^2$ year, with peak values occurring after 1970. After deconstruction of this total accumulation into components related to background values, values affected by land use (erosion), and focusing effects, the range of maximum accumulation rates is substantially reduced (10.4–66.3 $\mu\text{g Hg}/\text{m}^2$ year) and is temporally more coherent.

Recent values (ca. 1990) are nearly equal to, or greater than, those measured for 1998–2003 in wet deposition (NADP, 2004). NADP values (2003) are slightly less than 10 $\mu\text{g Hg}/\text{m}^2$ year, whereas Hg_A fluxes are 1–6 times this value. This comparison implies that at many lakes, the watershed supplies Hg to the lake in amounts in excess of wet deposition and likely in excess of modern wet plus dry deposition. Furthermore, Hg_A accumulation rates are typically 1–3 times Hg_B . Well-constrained data and modeling of sediment depositional processes enable a more complete picture of Hg emissions, transport, deposition, and storage within natural ecosystems.

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References

- Asmund, G. and Nielson, S. (2000). Mercury in dated Greenland marine sediments. *Sci. Total Environ.* **245**, 61–72.
- Appleby, P. and Oldfield, F. (1978). The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena* **5**, 1–8.
- Biester, H., Kilian, R., Franzen, C., Woda, C., Mangini, A. and Scholer, H. (2002). Elevated mercury accumulation in a peat bog of the Magellanic Moorlands, Chile (53 S) – an anthropogenic signal from the Southern Hemisphere. *Earth Planet. Sci. Lett.* **201**, 609–20.
- Bindler, R. (2003). Estimating the natural background atmospheric deposition rate of mercury utilizing ombrotrophic bogs in Southern Sweden. *Environ. Sci. Technol.* **37**(1), 40–6.
- Bindler, R., Renberg, I., Appleby, P., Anderson, N.J. and Rose, N. (2001a). Mercury accumulation rates and spatial patterns in Lake Sediments from West Greenland: a coast to Ice Margin Transect. *Environ. Sci. Technol.* **35**, 1736–41.
- Bindler, R., Olofsson, C., Renberg, I. and Frech, W. (2001b). Temporal trends in mercury accumulation in lake sediments in Sweden. *Water, Air Soil Pollution: Focus* **1**, 343–55.
- Boutron, C., Vandal, G., Fitzgerald, W. and Ferrari, C. (1998). A forty year record of mercury in central Greenland snow. *Geophys. Res. Lett.* **25**(17), 3315–18.
- Cumming, B.F., Glew, J.R., Smol, J.P., Davis, R.B. and Norton, S.A. (1993). Comment on “Core compression and surficial sediment loss of lake sediments of high porosity caused by gravity coring” (Crsius and Anderson). *Limnol. Oceanogr.* **38**(3), 695–9.
- Davis, R. and Doyle, R. (1969). A piston corer for upper sediment in lakes. *Limnol. Oceanogr.* **14**(4), 643–8.
- Dennis, I.F., Clair, T.A., Driscoll, C.T., Kamman, N.C., Chalmers, A., Shanley, J.B., Norton, S.A. and Kahl, S. (2005). Distribution patterns of mercury in lakes and rivers of northeastern North America. *Ecotoxicology* **14**(113–124).
- Eakins, J.D. and Morrison, R.T. (1978). A new procedure for the determination of lead-210 in lake and marine sediments. *Int. J. Appl. Radiation Isotopes* **29**, 531–6.
- Engstrom, D. and Swain, E. (1997). Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environ. Sci. Technol.* **31**, 960–7.
- Engstrom, D.R. and Wright, H.E. (1984). Chemical stratigraphy of lake sediments as records of environmental change. In E.Y. Haworth and J.W. Lund (eds). *Lake Sediments and Environmental History*, Minneapolis, MN: University of Minnesota Press.
- Evans, G.C., Norton, S.A., Fernandez, I.J., Kahl, J.S. and Hanson, D. Changes in concentrations of major and trace metals in northeastern U.S.–Canadian sub-alpine forest floors. *Water, Air Soil Pollution (in review)*.
- Frescholtz, T.F., Gustin, M.S., Schorran, D.E. and Fernandez, G.C.J. (2003). Assessing the source of mercury in foliar tissue of quaking aspen. *Environ. Toxicol. Chemistry* **22**, 2114–9.
- Gobeil, C., Macdonald, R.W. and Smith, J.N. (1999). Mercury profiles in sediments of the Arctic Ocean Basins. *Environ. Sci. Technol.* **33**, 4194–4198.
- Grigal, D. (2002). Inputs and outputs of mercury from terrestrial watersheds: a review. *Environ. Rev.* **10**(1), 1–39.
- Hermanson, M. (1998). Anthropogenic mercury deposition to Arctic lake sediments. *Water, Air Soil Pollution* **101**, 309–21.
- Iverfeldt, A. (1991). Mercury in forest canopy throughfall water and its relation to atmospheric deposition. *Water, Air, Soil Pollution* **56**, 553–64.
- Kamman, N. (2003). Paleolimnology of Lakes in the Vicinity of the Lye Brook Wilderness, Vermont, U.S.A.. ^{210}Pb Dating, Mercury and Carbon Isotopes. Report prepared for the US Forest Service, Green Mountain and Finger Lakes National Forest, and Vermont Monitoring Cooperative.
- Kamman, N. and Engstrom, D. (2002). Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from ^{210}Pb dated sediment cores. *Atmos. Environ.* **36**, 1599–609.
- Lamborg, C.H., Fitzgerald, W.F., Damman, W.H., Benoit, J.M., Balcom, P.H. and Engstrom, D.R. (2002). Modern and historic atmospheric mercury fluxes in both hemispheres: global and regional mercury cycling implications. *Global Biogeochem. Cycles* **16**(4), 51-1–51-11.
- Landers, D., Gubala, C., Verta, M., Lucotte, M., Johansson, K., Vlasova, T. and Lockhart, W. (1998). Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in arctic and boreal ecosystems. *Atmos. Environ.* **32**(5), 919–28.
- Lockhart, W., MacDonald, R., Outridge, P., Wilkinson, P., DeLaronde, J. and Rudd, J. (2000). Tests of the fidelity of lake sediment core records of mercury deposition to histories of mercury contamination. *Sci. Total Environ.* **260**, 171–80.
- Lockhart, W., Wilkinson, P., Billeck, B., Danell, R., Hunt, R., Brunskill, G., Delaronde, J. and Louis, V.St (1998). Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry* **40**, 163–73.
- Lorey, P. and Driscoll, C. (1999). Historical trends of mercury deposition in Adirondack lakes. *Environ. Sci. Technol.* **33**, 718–22.
- Lucotte, M., Mucci, A., Hillaire-Marcel, C., Pichet, P. and Grondin, A. (1995). Anthropogenic mercury enrichment in remote lakes of northern Quebec (Canada). *Water, Air Soil Pollution* **80**, 467–76.
- MacKenzie, A.B., Logan, E.M., Cook, G.T. and Pulford, I.D. (1998). A historical record of atmospheric depositional fluxes of contaminants in west-central Scotland derived from an ombrotrophic peat core. *Sci. Total Environ.* **222**(3), 157–66.
- Martínez-Cortizas, A., Pontevedra-Pombal, X., García-Rodeja, E., Shotyk, W. (1999). Mercury in a Spanish peat bog: archive of climate change and atmospheric metal deposition. *Science* **284**, 939–42.

- Meili, M. (1995). Pre-industrial atmospheric deposition of mercury: uncertain rates from lake sediment and peat cores. *Water, Air Soil Pollution* **80**, 637–40.
- Munthe, J., Kindbom, K., Kruger, O., Petersen, G., Pacyna, J. and Iverfeldt, Å. (2001). Examining source–receptor relationships for mercury in Scandinavia. *Water, Air Soil Pollution: Focus* **1**, 299–310.
- National Atmospheric Deposition Network (NADP). (2004). <http://nadp.sws.uiuc.edu/mdn/>.
- Norton, S.A., Bienert, R.W. Jr., Binford, M.W. and Kahl, J.S. (1992). Stratigraphy of total metals in PIRLA sediment cores. *J. Paleolimnol.* **7**, 191–214.
- Norton, S., Evans, G. and Kahl, S. (1997). Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to nearby Sargent Mt. Pond, Maine U.S.A.. *Water, Air Soil Pollution* **100**, 271–86.
- Norton, S.A., Perry, E., Haines, T.A. and Dieffenbacher-Krall, A. (2004). Paleolimnological assessment of grove and plow shop ponds, Fort Devens-Ayer, Massachusetts. *J. Environ. Monitor.* **6**, 1–11.
- Perry, E., Norton, S., Cangelosi, J., Hess, C. and Norris, M. (2001). Mercury storage, release and transport in the watersheds of seven Maine lakes. Geological Society of America, Northeast Section, *Program with Abstracts*.
- Pilgrim, W., Poissant, L. and Trip, L. (2000). The Northeast States and Eastern Canadian Provinces mercury study: a framework for action: summary of the Canadian chapter. *Sci. Total Environ.* **261**, 177–84.
- Pirrone, N., Allegrini, I., Keeler, G., Nriagu, J., Rossman, R. and Robbins, J. (1998). Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. *Atmos. Environ.* **32**(5), 929–40.
- Roos-Barraclough, F., Martínez-Cortizas, A., Shotyk, W. (2002). A 14,500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. *Earth Planet. Sci. Lett.* **202**, 435–51.
- Schroeder, W. and Munthe, J. (1998). Atmospheric Mercury: an overview. *Atmos. Environ.* **32**(5), 809–22.
- Schuster, P.F., Krabbenhoft, D.P., Naftz, D.L., Cecil, D., Olson, M.L., Dewild, J.F., Susong, D.D., Green, J.R. and Abbott, M.L. (2002). Atmospheric mercury deposition during the last 270 years: a glacial ice core record of natural and anthropogenic sources. *Environ. Sci. Technol.* **36**, 2303–10.
- Shanley, J.B., Kamman, N.C., Clair, T.A. and Chalmers, A. (2005). Physical controls on total and methylmercury concentrations in streams and lakes of the northeastern USA. *Ecotoxicology* **14**(125–134).
- Shanley, J.B., Kendall, C., Smith, T.E., Wolock, D.M. and McDonnell, J.J. (2002a). Controls on old and new water contributions to stream flow at some nested catchments in Vermont U.S.A.. *Hydrol. Process.* **16**(3), 589–609.
- Shanley, J.B., Schuster, P.F., Reddy, M.M., Roth, D.A., Taylor, H.E. and Aiken, G.R. (2002b). Mercury on the move during snowmelt in Vermont. *EOS* **83**, 45 and 47.
- Shotyk, W., Goodsite, M.E., Roos-Barraclough, F., Givélet, N., LeRoux, G., Weiss, D., Chebruquin, A.K., Knudsen, K., Heinemeier, J., van der Knaap, W.O., Norton, S.A. and Lohse, C. (2004). Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands since 5420 ¹⁴C yr BP recorded by a peat core from a blanket bog. *Geochimica Cosmochimica Acta* **69**, 1–17.
- Swain, E., Engstrom, D., Brigham, M., Henning, T. and Brezonik, P. (1992). Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* **257**, 784–6.
- Trip, L. and Allan, R. (2000). Sources, trends implications and remediation of mercury contamination of lakes in remote areas of Canada. *Water Sci. Technol.* **42**(7–8), 171–4.
- Wängberg, I., Munthe, J., Pirrone, N., Iverfeldt, Å., Bahlman, E., Costa, P., Ebinghaus, R., Feng, X., Ferrara, R., Gårdfeldt, K., Kock, H., Lanzillotta, E., Mamane, Y., Mas, F., Melamed, E., Osnat, Y., Prestbo, E., Sommar, J., Schmolke, S., Spain, G., Sproveiri, F. and Tuncel, G. (2001). Atmospheric mercury distribution in Northern Europe and in the Mediterranean region. *Atmos. Environ.* **35**, 3019–25.
- Yang, H. and Rose, N. (2003). Distribution of mercury in six lake sediment cores across the UK. *Science Total Environ.* **304**, 391–404.