

History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition

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Abstract

The history of mercury (Hg) inputs to 55 Minnesota (U.S.A.) lakes was reconstructed from ²¹⁰Pb (lead-210)-dated sediment cores to determine if erosion of soils from agriculture and urbanization contributes a significant loading of Hg to lakes, and whether lakes near Hg-emitting facilities receive appreciable local atmospheric deposition. Modern (1994–1997) Hg accumulation and Hg flux ratios (modern:preindustrial) increase significantly with the percentage of watershed area under urban or agricultural land-use. Both past and modern Hg accumulation rates are strongly correlated with the flux of total aluminum (Al), a tracer for soil erosion. Modern Hg accumulation rates are substantially higher in the Minneapolis–St. Paul metropolitan area and in agriculturally dominated south-central Minnesota than in the forested northeastern part of the state, largely because of erosional inputs of soil-bound Hg from disturbed catchments. Modern Hg loading from direct atmospheric deposition is also greater in the metropolitan region than in the rural areas of south-central or northeastern Minnesota. However, some of the excess loading to urban lakes may also be a legacy of formerly high Hg deposition to urban watersheds. A decline in local Hg emissions from peak levels in the 1970s coupled with reduced erosional inputs has cut Hg loading to many metro-area lakes by more than half.

Mercury (Hg) released to the atmosphere and surface waters from human activities is a serious environmental problem, because even trace amounts can bioaccumulate to harmful levels in fish and upper levels of the aquatic food chain. Where Hg loading is dominated by atmospheric sources, it is thought that the degree of Hg accumulation in fish is roughly proportional to the long-term rate of atmospheric Hg deposition, other factors being equal (Munthe et al. 2007). In areas where wide-spread Hg contamination of fish has been documented, such as Minnesota, U.S.A. (Minnesota Pollution Control Agency [MPCA] 2007; Wiener et al. 2006), the site of this study, it is therefore useful to determine to what degree Hg loading has changed over time and to what extent those changes are a result of changes in atmospheric Hg deposition as compared to land use.

Hg emitted to the atmosphere from both anthropogenic and natural sources may be dispersed widely and deposited

far from any emissions sources (Fitzgerald et al. 1998). Atmospheric Hg deposition in remote locations has increased continuously over the past 200 yr, and the present rate of deposition is two to four times the historic (preindustrial) level (Lockhart et al. 1998; Bindler et al. 2001; Lamborg et al. 2002; Lindberg et al. 2007). Mercury deposition in rural Minnesota is elevated three-fold over preindustrial levels, and in pristine (forested and undeveloped) watersheds, a small portion (<20%) of the Hg deposited to terrestrial catchments makes its way into lakes; the remainder is retained in the soils or reemitted to the atmosphere (Swain et al. 1992; Engstrom et al. 1994). One of our working hypotheses is that preindustrial Hg deposition was essentially uniform across Minnesota. Recently, a study of urban lakes in the city of Minneapolis showed that peak Hg inputs to these sites were elevated 9–16 times above preindustrial levels—well above the increase in rural Minnesota (Engstrom and Swain 1997). These results suggest that Hg deposition in the Minneapolis–St. Paul metropolitan area may be higher than in rural areas or that disturbed watersheds (urban or agricultural) are much less effective in retaining Hg than are forested ones. Accordingly, a second working hypothesis is that modern atmospheric deposition is broadly uniform across the state with the possible exception of the Minneapolis–St. Paul area. This paper examines sediment core data for exceptions from that generality over time and space, with the understanding that Hg flux to a lake is a function of both atmospheric deposition and export from the lake's terrestrial watershed.

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Land use exerts a major influence on Hg export from watersheds (Hurley et al. 1995; Grigal 2002), and land-use changes that increase rates of soil erosion could be expected to enhance the flux of Hg to lakes. Recent mass-balance studies suggest that Hg yields from urban and agricultural watersheds may greatly exceed those from forested catchments (Balogh et al. 1998, 2005; Lockhart et al. 1998; Mason and Sullivan 1998). Moreover, much of the Hg transported from these disturbed watersheds moves during storm events and is associated with high loads of soil-derived suspended sediment. One focus of the research reported here is to characterize the influence of watershed disturbance on the export of Hg from catchment soils to downstream aquatic environments.

A second focus of this research is to determine whether certain regions of Minnesota have experienced larger anthropogenic increases in atmospheric Hg deposition than others. Direct measurement of Hg deposition (Iverfeldt 1991; Hoyer et al. 1995) and indirect studies of Hg accumulation in lake sediments, peat, and soils (Johansson 1985; Steinnes and Andersson 1991; Nater and Grigal 1992) show clear spatial gradients of higher Hg loading near Hg emission sources in industrialized areas of North America and Europe. Although the Minneapolis–St. Paul metropolitan area (2000 population = 2.64 million) has never supported large industrial Hg emitters (e.g., smelters, chlor-alkali plants), it is possible that the combined emissions from light industry, power-plants, waste incineration, vehicular emissions, and residential heating provide an additional load to the urban Hg flux. Several isolated point-source Hg emitters including coal-fired boilers, waste incinerators, and taconite-processing plants could also contribute to higher Hg deposition in parts of northeastern Minnesota. It is reasonable, then, to ask whether Hg deposition gradients occur today (or did historically) across Minnesota, for if they do it would suggest that Hg deposition could be lowered by emission reductions at the local or regional scale.

In this study, we evaluate recent changes in Hg inputs to lakes in three regions of Minnesota that are characterized by different types of land use and proximity to Hg emission sources. Trends in atmospheric deposition and watershed inputs are inferred from Hg accumulation rates in ^{210}Pb -dated sediment cores from 20 lakes in the Minneapolis–St. Paul metropolitan area (Metro region), 15 lakes in the agricultural parts of south-central Minnesota, and 20 lakes from the forested regions of northeastern Minnesota. By comparing Hg accumulation trends among these different areas, we are able to separate changes in Hg inputs resulting from atmospheric Hg deposition from those caused by local land-use practices.

Methods

Site selection—Study lakes (Fig. 1) were selected from each of three regions (Metro, South Central, and Northeast) in Minnesota, based on criteria that included: (1) adequate depth for conformable sedimentation, (2) relatively small watershed with no inflows from large rivers, (3) availability of historical water quality and fish-Hg data, (4)

absence of local Hg point-source discharges, and (5) absence of recent manipulations that might alter sedimentation patterns within the lake (e.g., dredging, lake-level changes). In metropolitan and south-central Minnesota, lakes were also chosen to represent the range of water quality (trophic) conditions and land-use cover types for those regions. Lakes in northeastern Minnesota were clustered in four subregions based on proximity to local Hg emission sources.

GIS analysis—Watershed and lake-surface areas, land cover, and topography were quantified by high-resolution Geographic Information Systems (GIS) analysis. Landscape features were digitized using ArcEdit Environmental Systems Research Institute (ESRI) and a U.S. Geological Survey (USGS) Panchromatic Digital Orthophoto Quarter Quad (DOQQ) as a background image. Watershed boundaries were initially delineated on USGS 7.5-min series topographic quadrangles for each of the study lakes and then fine-tuned against elevation values from USGS 30-m Digital Elevation Models (DEMs). Land cover was interpreted from early spring 1991–1992 Color Infrared (CIR) National Aerial Photography Program (NAPP) photographs based on a modified USGS classification scheme (Anderson et al. 1976). Cover types were later grouped into six general categories (forest, agriculture, built-up, wetland, open water, and road) for comparison with Hg trends. Approximately 50% of the watersheds in the study were spot-field-checked for classification accuracy.

Core collection—A piston corer equipped with a 7-cm-diameter polycarbonate core barrel and operated from the lake surface by magnesium-alloy drive-rods was used to collect a continuous 1–2-m section of the upper sediments from each lake (Wright 1991). Cores were collected from 1995 to 1997. Core sites were carefully located by sonar and bathymetric maps in deep flat areas of the basin, distant from any steep slopes that might be subject to slumping. Cores were extruded vertically at 1–5-cm increments into acid-washed polypropylene collection jars on shore and stored at 4°C until further processing.

Loss-on-ignition and geochemistry—Dry-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate content of sediments were determined by standard loss-on-ignition techniques (Heiri et al. 2001). Sediment samples of 1–2 g were dried overnight at 100°C and ignited at 550°C and 1,000°C for 1 h each. Mass measurements were made of the wet samples and after each heating on an electronic analytical balance. Dry density was calculated from water content and fixed densities for organic, carbonate, and inorganic fractions. Selected intervals representing recent (core-top) and pre-industrial periods were analyzed for major element geochemistry by lithium borate fusion and inductively coupled plasma mass spectrometry (ICP-MS).

Lead-210 dating—All cores were analyzed for ^{210}Pb activity to determine age and sediment accumulation rates

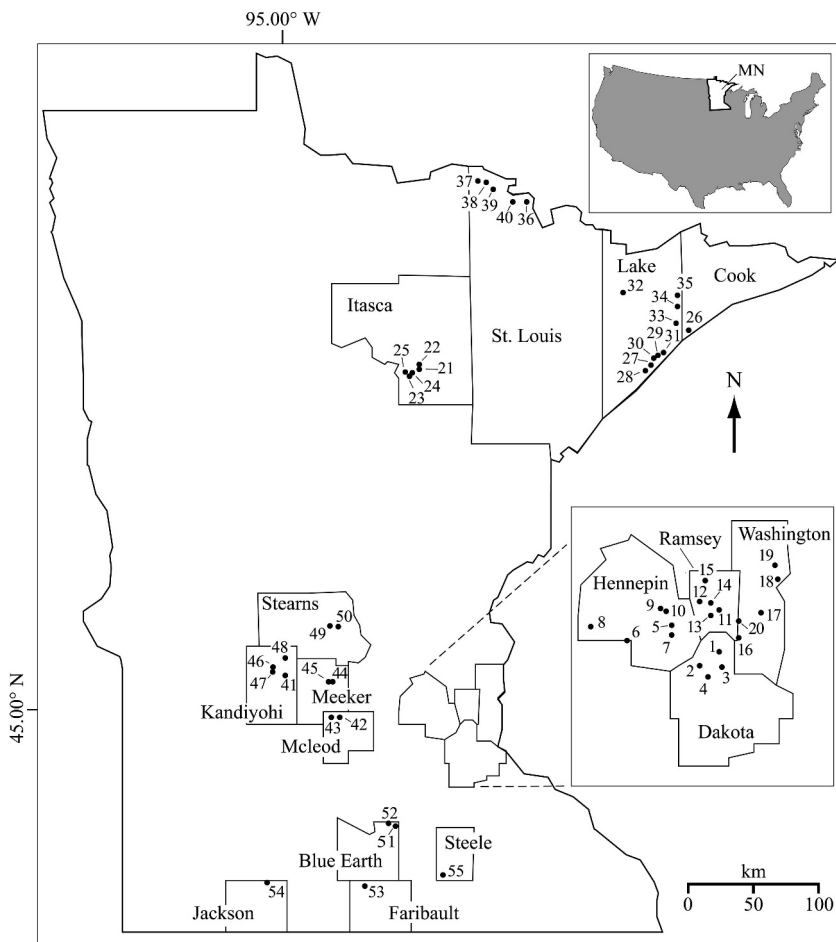


Fig. 1. Location of study lakes in Minnesota, USA; only those counties with lakes are shown; key to lake names in Table 1. Lake groups by region: (1–20) Metro = Minneapolis–St. Paul metropolitan area, (21–40) North = northeastern Minnesota, and (41–55) South = south-central Minnesota (rural).

for the past 150–200 yr. Lead-210 was measured at 15–23 depth intervals in each core through its grand-daughter product ^{210}Po , with ^{209}Po added as an internal yield tracer. The polonium isotopes were distilled from 1.5 g to 7.0 g dry sediment at 550°C following pretreatment with concentrated hydrochloric acid (HCl), and plated directly onto silver planchets from a 0.5-mol L^{-1} HCl solution (Eakins and Morrison 1978). Activity was measured for $1\text{--}3 \times 10^5$ s with ion-implanted or silicon-depleted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported ^{210}Pb was calculated by subtracting supported activity from the total activity measured at each level; supported ^{210}Pb was estimated from the asymptotic activity at depth (the mean of the lowermost samples in a core). Dates and sedimentation rates were determined according to the c.r.s. (constant rate of supply) model with confidence intervals calculated by first-order error analysis of counting uncertainty (Appleby 2001). Except as noted, sedimentation rates were not corrected for sediment focusing, as is sometimes done based on the inventory of ^{210}Pb in a core (e.g., Lockhart et al. 1998), because many of the Metro and South Central lakes receive a substantial load of excess ^{210}Pb from soil erosion caused by urban and

agricultural land-use (S. P. Schottler and D. R. Engstrom, unpubl. data).

Mercury—Total Hg was determined in freeze-dried sediment samples from each core. Subsamples (0.1 g) were digested in 10 mL concentrated nitric acid:sulfuric acid ($\text{HNO}_3:\text{H}_2\text{SO}_4$; 70:30 v:v) at 65°C for 4 h in rigorously acid-leached 60-mL Teflon® (DuPont) vials. Samples were cooled, then 6 mL potassium permanganate (KMnO_4 ; 5% w/v) and 3 mL potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$; 5% w/v) were added and the digestion continued at 65°C for 2 more hours. Digestate volume was brought to 25 mL with distilled deionized water, and Hg was determined on an aliquot of the digestate using cold-vapor atomic fluorescence with single gold-trap amalgamation (Liang and Bloom 1993). Two different reference materials (BCR-320 River Sediment and BCSS-1 Marine Sediment) were typically analyzed with each core. The mean concentration of Hg in BCR-320 was determined to be 930 ng g^{-1} ($n = 56$; relative standard deviation (RSD) = 9%; certified value = $1,030\text{ ng g}^{-1}$). The mean concentration of Hg in BCSS-1 was determined to be 170 ng g^{-1} ($n = 50$; RSD = 4%; accepted value = 176 ng g^{-1} [Willie and Berman 1995]).

Table 1. Geographic and chemical characteristics of the study lakes in Minnesota, USA.

Lake	County	Map No.	Lat. N (0.000°)	Long. W (0.000°)	Lake* (km ²)	Catchment† (km ²)	Built-up‡ (%)	Ag-land‡ (%)	Forest‡ (%)	pH	Alk (meq L ⁻¹)	DOC (mg L ⁻¹)	Total-P (µg L ⁻¹)
Metro region													
Dickman	Dakota	1	44.862	93.079	0.09	0.57	38.3	10.3	31.2	7.89	1.48	7.9	105
Fish	Dakota	2	44.823	93.167	0.12	15.06	70.6	8.8	10.0	7.59	1.61	7.7	79
Marcott	Dakota	3	44.816	93.067	0.07	2.51	20.4	12.3	33.4	7.76	2.39	6.9	19
Schultz	Dakota	4	44.785	93.129	0.05	0.69	0.5	1.0	57.3	7.80	1.69	7.6	26
Calhoun	Hennepin	5	44.944	93.313	1.69	25.15	88.1	0.0	3.4	8.70	2.15	6.1	22
Christmas	Hennepin	6	44.898	93.541	1.06	1.89	85.6	2.0	5.2	8.90	2.62	6.2	11
Harriet	Hennepin	7	44.919	93.310	1.39	3.87	90.5	0.0	8.2	8.90	2.09	5.7	13
Little Long	Hennepin	8	44.948	93.708	0.22	0.32	0.0	18.0	58.0	8.80	1.68	6.2	10
Sweeney	Hennepin	9	44.991	93.341	0.28	10.11	93.1	0.0	3.5	8.38	4.20	5.5	46
Twin	Hennepin	10	44.992	93.336	0.09	0.33	35.8	0.0	58.3	8.55	2.93	7.5	22
Gervais	Ramsey	11	45.017	93.072	0.94	40.28	80.3	0.0	3.2	8.32	2.32	7.2	51
Johanna	Ramsey	12	45.040	93.166	0.86	10.26	86.9	0.0	3.4	8.25	1.62	7.1	46
McCarrons	Ramsey	13	44.997	93.111	0.30	4.12	82.2	0.0	5.7	8.60	1.59	8.8	39
Owasso	Ramsey	14	45.038	93.124	1.51	4.23	84.4	0.0	2.2	8.15	2.03	8.1	36
Turtle	Ramsey	15	45.104	93.136	1.33	1.80	80.0	0.0	0.0	8.26	2.32	7.7	20
Carver	Washington	16	44.906	92.981	0.20	8.64	52.4	18.2	11.7	8.70	2.19	7.1	38
Elmo	Washington	17	44.989	92.883	1.15	20.76	31.1	42.8	9.0	8.50	2.87	6.4	10
L. Carnelian	Washington	18	45.118	92.796	0.47	18.54	7.7	41.2	23.3	8.80	2.12	5.7	9
Square	Washington	19	45.157	92.804	0.82	2.26	14.0	20.4	45.8	8.70	2.43	3.8	6
Tanners	Washington	20	44.950	92.981	0.30	6.69	79.6	0.0	2.0	8.90	2.37	8.6	36
Northeast region													
Forsythe	Itasca	21	47.266	93.601	0.27	1.91	0.0	5.1	50.3	6.89	0.23	13.9	21
Little Bass	Itasca	22	47.284	93.602	0.64	5.40	4.7	10.9	61.1	8.16	2.42	8.2	13
Long	Itasca	23	47.227	93.657	0.55	1.65	0.2	8.5	72.2	8.08	2.29	8.1	13
Loon	Itasca	24	47.232	93.640	0.93	3.64	2.9	12.3	57.7	8.55	2.47	8.0	11
Snells	Itasca	25	47.241	93.677	0.36	2.88	0.0	43.3	49.7	8.18	2.51	10.7	24
Dyers	Cook	26	47.527	90.980	0.28	8.54	0.0	0.0	92.2	7.57	0.69	9.7	27
Bean	Lake	27	47.309	91.300	0.12	0.64	0.0	0.0	91.0	7.64	0.53	4.5	17
Bear	Lake	28	47.284	91.344	0.18	0.60	0.0	0.0	89.2	7.45	0.34	3.8	11
Nipisiquit	Lake	29	47.355	91.249	0.24	2.98	0.0	0.0	100.0	7.40	0.49	5.9	16
Tettegouche	Lake	30	47.344	91.270	0.27	1.03	0.0	0.0	100.0	7.32	0.30	7.3	17
Wolf	Lake	31	47.377	91.193	0.13	0.68	0.0	0.0	79.4	7.76	0.61	5.0	14
August	Lake	32	47.763	91.606	0.76	9.37	0.0	0.0	96.5	7.25	0.29	12.6	15
Ninemile	Lake	33	47.576	91.081	1.20	2.09	0.0	0.0	83.2	7.39	0.36	6.7	17
Wilson	Lake	34	47.674	91.076	2.57	7.19	0.0	0.0	78.0	7.45	0.34	4.8	13
Windy	Lake	35	47.735	91.072	1.85	17.05	5.6	0.0	91.9	6.94	0.15	12.6	12
Little Trout	St. Louis	36	48.395	92.527	1.08	1.40	0.0	0.0	100.0	7.37	0.31	4.4	7
Locator	St. Louis	37	48.541	93.006	0.54	14.89	0.0	0.0	83.9	6.99	0.12	10.8	9
Loiten	St. Louis	38	48.527	92.927	0.39	2.42	0.0	0.0	93.8	7.05	0.15	8.7	8
Shoepack	St. Louis	39	48.497	92.888	1.55	17.68	0.0	0.0	74.7	6.59	0.10	14.3	19
Tooth	St. Louis	40	48.398	92.643	0.24	1.51	0.0	0.0	90.1	6.84	0.19	10.0	12
South central region													
Diamond	Kandiyohi	41	45.186	94.854	6.45	35.90	4.1	74.4	5.6	8.55	3.36	7.9	80
Hook	McLeod	42	44.954	94.341	1.33	6.20	41.0	6.7	30.3	8.44	2.95	12.0	68
Stahl	McLeod	43	44.953	94.421	0.55	6.30	35.7	27.5	11.4	8.39	3.11	11.7	46

Table 1. Continued.

Lake	County	Map No.	Lat. N (0.000°)	Long. W (0.000°)	Lake* (km ²)	Catchment† (km ²)	Built-up‡ (%)	Ag-land‡ (%)	Forest‡ (%)	pH	Alk (meq L ⁻¹)	DOC (mg L ⁻¹)	Total-P (µg L ⁻¹)
Dunns	Meeker	44	45.158	94.429	0.63	13.81	16.3	35.3	32.7	8.64	2.23	10.3	139
Richardson	Meeker	45	45.160	94.440	0.48	11.68	2.9	76.4	5.6	8.29	2.72	8.5	98
George	Kandiyohi	46	45.243	94.984	0.92	1.02	0.0	57.7	14.5	8.82	4.55	6.4	15
Henderson	Kandiyohi	47	45.230	94.993	0.29	0.59	3.4	72.6	5.4	8.61	4.18	8.3	22
Long	Kandiyohi	48	45.331	94.852	1.30	3.63	2.5	76.1	4.2	8.46	3.41	4.9	19
Kreighle	Stearns	49	45.579	94.478	0.41	0.88	0.0	23.0	71.3	8.50	2.01	6.9	11
Sagatagan	Stearns	50	45.574	94.391	0.89	2.52	2.4	22.0	58.7	8.45	1.74	7.2	27
Duck	Blue Earth	51	44.218	93.815	1.17	3.85	3.9	86.3	1.7	8.91	2.89	9.4	65
George	Blue Earth	52	44.234	93.871	0.36	0.54	0.0	81.2	18.4	9.18	1.98	11.8	130
Bass	Faribault	53	43.820	94.078	0.76	1.36	14.7	69.7	10.5	8.96	3.34	9.5	81
Fish	Jackson	54	43.847	95.044	1.21	6.49	1.8	90.1	3.8	8.82	3.25	7.4	38
Beaver	Steele	55	43.892	93.348	0.38	0.71	14.5	60.8	23.9	8.86	2.50	9.8	30

* Lake-surface area.

† Catchment area excluding lake surface.

‡ Portion of catchment in different land-use classes: Built-up = residential-urban; Ag-land = agricultural (row-crop, dairy); Forest = all forest types.

One sample from each core was analyzed in triplicate, and one matrix spike sample was run with each core. The mean matrix spike recovery was 101% ($n = 55$; RSD = 6%), and the mean RSD of the triplicate analyses was 3% ($n = 55$). All samples had total Hg concentrations well above our method detection limit of 0.6 ng g⁻¹ (3 times the standard deviation of our reagent blank determinations [$n = 55$]).

Results

Study sites—Twenty of the lakes are located within the greater metropolitan area of Minneapolis and St. Paul (Fig. 1, Table 1). Roughly half of the lakes in this Metro group are embedded in urban neighborhoods within a radius of 10 km of the centers of either of the two cities, while the other half are located in rural landscapes more distant from the urban core. A second group of 20 lakes occurs across a tier of four counties in northeastern Minnesota. Five of these Northeast lakes are tightly clustered near the city of Grand Rapids in Itasca County, while another five are located within Voyageurs National Park near the U.S.–Canadian border in St. Louis County. The Northeast group of lakes are among the most pristine in the 55-lakes data set and have little or no human development within their watersheds. A third group of 15 lakes is situated within the largely agricultural landscape of south-central Minnesota. Ten of these South Central lakes have relatively large, agriculturally dominated watersheds and are of poor water quality, while the other five have small watersheds, high water quality, and less agricultural influence. All of the lakes are rural, and many are ringed with summer cottages and lake homes.

The study lakes range in size from 0.05 km² to 6.45 km², although only two of the lakes exceed 2 km² (Table 1). Lake surface areas are similar for the Metro and Northeast groups (median area = 0.38 and 0.47 km², respectively) and only slightly larger for the South Central group (median = 0.76 km²). Maximum lake depth for the entire data set ranges from 2.4 m to 42.7 m, and the distribution of depths is broadly similar among the three regions. Total catchment area (excluding lake surface) for the 55 study sites ranges from 0.32 km² to 40.28 km², with catchments in the Northeast group being somewhat smaller and more tightly grouped (median = 2.65 km²) than those in the Metro area (median = 4.18 km²) or South Central region (median = 3.63 km²). The ratio of total-catchment to lake-surface area for the entire data set ranges from 1.1 to 120.8 with a median value of 5.6.

The chemistry of the study lakes, which stratifies very clearly by region, reflects both the underlying geological differences and contrasts in prevailing land use among the three major lake groups (Table 1). The Northeast lakes, which lie mostly in thin, noncarbonate glacial drift and crystalline bedrock, are characterized by low alkalinity (median = 0.34 meq L⁻¹) and circumneutral pH (median = 7.4). In contrast, the Metro and South Central lakes are situated in thick carbonate-rich drift and have a median pH of 8.5 and alkalinities in excess of 1.5 meq L⁻¹. The three lake groups also differ with respect to trophic conditions, with the Northeast lakes characterized by lower total-P

(mean \pm 1 SD = $15 \pm 5 \mu\text{g L}^{-1}$), than the Metro ($32 \pm 25 \mu\text{g L}^{-1}$) or the South Central lakes ($59 \pm 43 \mu\text{g L}^{-1}$).

Core lithology and dating—The collected sediment cores ranged in length from 0.8 m to 2.0 m, and in all cases extended well into older strata of preindustrial age. The cores from the Metro and South Central lakes usually revealed a sharp change in sediment composition from a black, sapropelic mud or dense gray silt to a brown gyttja somewhere deep in the profile (Web Appendix 1, www.aslo.org/lo/toc/vol_52/issue_6/2467a1.pdf). This lithologic transition, which was almost always accompanied by a change in organic matter and carbonate content, marked the onset of European settlement within the local catchment. This “settlement horizon” was a valuable aid in core sectioning and sample selection and helped confirm the results of ^{210}Pb dating.

Stratigraphic profiles of total ^{210}Pb range from near exponential (many Northeast lakes) to highly kinked and nonmonotonic (Web Appendix 2, www.aslo.org/lo/toc/vol_52/issue_6/2467a2.pdf). The exponential profiles from the Northeast lakes indicate constant sediment accumulation, while the flat sections and reversals, evident in most of the Metro and South Central profiles, suggest major changes in sediment input over the last 150 yr. All but two cores could be reliably dated by the c.r.s. (constant rate of supply) model, and few of the ^{210}Pb profiles show evidence of sediment mixing sufficient to affect the resulting chronologies. In most of the cores, dating precision was better than ± 5 yr (1 SD) for the last century and ± 2 – 3 yr for the most recent 50 yr. However, dates for the preindustrial period have much higher uncertainty, especially for Metro and South Central lakes. For the Northeast lakes, the median error for pre-1860 dates was ± 10 yr, whereas for the Metro and South Central lakes the uncertainty was ± 16 yr. The better dating control for the Northeast lakes arises because unsupported ^{210}Pb activities are higher in these cores and can be estimated above background (supported ^{210}Pb) with greater precision.

Sediment accumulation—Almost all of the lakes in the data set show some increase in sediment accumulation that began with the onset of local land-use change and European settlement (Web Appendix 3, www.aslo.org/lo/toc/vol_52/issue_6/2467a3.pdf). Among Metro area lakes the rise in sediment flux began sometime after 1860 and was gradual at first. Sediment accumulation accelerated dramatically after the turn of the century and reached peak values (3–20 times presettlement rates) during the 1940s and 1950s. During the last two decades, sediment flux has declined sharply in 14 of the 20 Metro lakes. The increase in sediment accumulation among South Central lakes is similar in timing and magnitude to the Metro group, although seven of the 15 lakes in this region show a rising flux right up to the present decade. Six others show a drop from peak values during the last 20–40 yr, while two reveal no trend over the period of record. Sixteen of the 20 Northeast lakes also show an increase in sediment accumulation, but one that is later and smaller than in the Metro and South Central groups. In most cores the

increase occurs after 1900, probably in response to logging, and modern accumulation rates are about double those of the previous century. Lakes from Voyageurs National Park exhibit the smallest change in sediment flux among any in the data set, with three of the lakes essentially constant over time.

Present-day sediment accumulation rates in the 55-lake data set span about two orders of magnitude, ranging from $0.05 \text{ kg m}^{-2} \text{ yr}^{-1}$ to $5.0 \text{ kg m}^{-2} \text{ yr}^{-1}$ (Fig. 2). With a median value of $1.55 \text{ kg m}^{-2} \text{ yr}^{-1}$, the South Central lakes are among the highest, although there is considerable overlap with the Metro group (median = $0.55 \text{ kg m}^{-2} \text{ yr}^{-1}$), but little with the Northeast lakes (median = $0.22 \text{ kg m}^{-2} \text{ yr}^{-1}$). These values represent an average increase over preindustrial (pre-1860) sedimentation rates of 500%, 340%, and 100% for the South Central, Metro, and Northeast groups, respectively. Within the Northeast group, those lakes in Voyageurs National Park have the lowest sediment accumulation rates, both modern (median = $0.08 \text{ kg m}^{-2} \text{ yr}^{-1}$) and preindustrial (median = $0.05 \text{ kg m}^{-2} \text{ yr}^{-1}$), and the smallest average increase from preindustrial to modern. Sediment accumulation rates for the 20th century have a mean error of 6% (1 SD), whereas those representing the preindustrial period (pre-1860) have a much higher uncertainty (mean = 31%). The pre-1860 errors for the Metro and South Central cores are even greater (mean = 49%).

Mercury—Concentrations of Hg increase in most cores from a low background in preindustrial sediments (pre-1860) to maximum values sometime during the 20th century (Figs. 3–5). In many cases the rise is nonmonotonic; some cores show a reversal during the mid-1900s (e.g., Fish, McCarrons), others decline from peak values during the last few decades (e.g., Square, Harriet), and a few show no increase at all (e.g., Hook, Stahls). These concentration trends are strongly influenced by the rate of sediment accumulation which functionally dilutes the incoming Hg. Thus, the large spikes in 20th century sediment flux in many of the metro cores (e.g., Fish, Gervais, McCarrons) coincide closely with minima in Hg concentration (Fig. 3). Likewise those South Central cores showing a major rise in postsettlement sediment flux (e.g., Hook, Stahls, Dunns) have steadily declining Hg concentrations during the same period (Fig. 5). Although Hg concentrations commonly fall during periods of increased sediment flux, the accumulation of Hg almost always rises.

Differences in Hg concentrations are also closely aligned with rates of sediment accumulation both within and among lake groups. Sedimentary Hg concentrations are consistently higher in the Northeast group of lakes than in the South Central and Metro lakes, both in preindustrial (pre-1860) and modern (post-1994) times (Fig. 2). The median preindustrial Hg concentration in the Northeast lakes (106 ng g^{-1}) is higher than any of the preindustrial values from either the Metro or South Central groups (medians = 41 and 45 ng g^{-1} , respectively), and the same is true for modern Hg concentrations (medians = 186, 102, and 52 ng g^{-1} , for Northeast, Metro, and South Central, respectively). Conversely, sediment accumulation rates are

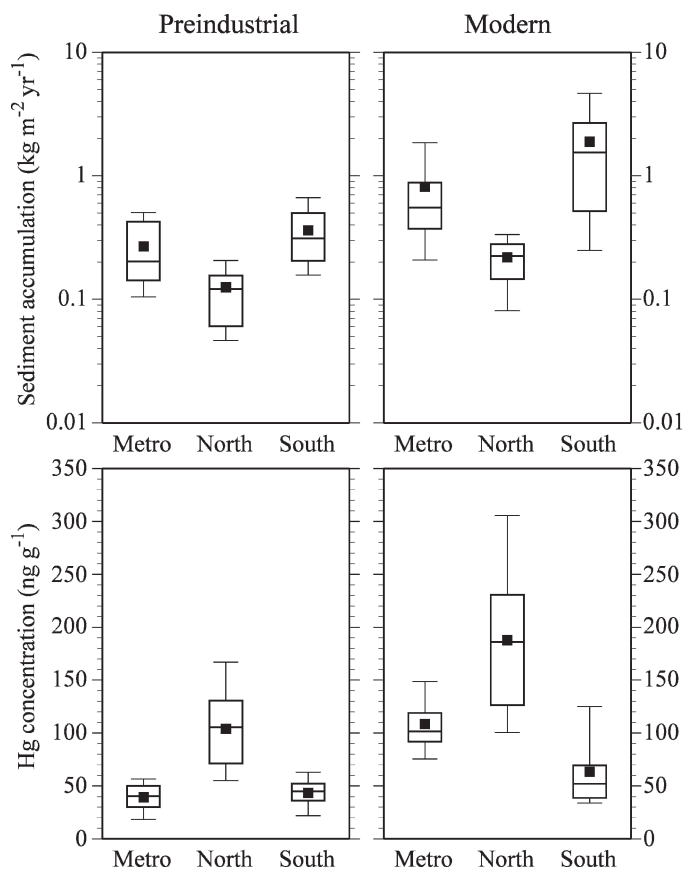


Fig. 2. Box plots of sediment accumulation rates and total mercury (Hg) concentrations and accumulation rates for 55 study lakes by region; Metro = Minneapolis–St. Paul metropolitan area, North = northeastern Minnesota (USA), South = south-central Minnesota (rural). Boxes represent interquartile ranges, bars delineate upper and lower 10%, and the center line is the median; means are shown by closed squares.

lowest in the Northeast lakes. The South Central lakes, which show the smallest increase in Hg concentrations between preindustrial and modern times, also have the largest increase in sediment flux between these two periods. Thus, the consistently negative covariance between sediment flux and Hg concentration indicates that most sediment sources are generally depleted in Hg and act as a dilutant to atmospheric Hg inputs.

In the Lake Elmo core (Fig. 3), an unusually large spike in Hg concentration during the 1930s indicates Hg contamination well in excess of that which could be supplied from the atmosphere. Peak concentrations ($2,100 \text{ ng g}^{-1}$) and accumulation rates ($2,700 \mu\text{g m}^{-2} \text{ yr}^{-1}$) for Hg exceed maximum values in most other cores by an order of magnitude. Although this peak was of relatively short duration (1910–1940), surface Hg concentrations (220 ng g^{-1}) and fluxes ($480 \mu\text{g m}^{-2} \text{ yr}^{-1}$) remain elevated compared to other metro sites. The most likely explanation for these historically enriched sediments is use of Hg at a nearby dairy plant that had a direct discharge to Lake Elmo (D. Hall, MPCA, pers. comm.). Although we have no specific evidence of Hg use, prior to the 1940s mercuric chloride (known as “corrosive sublimate”) was the preferred additive to preserve milk at

dairies for the later measurement of butterfat (Newlander 1916; Jackson 1919). Once the butterfat was measured, it seems likely that the dairy would dispose of the sample in their wastewater. The likelihood of a local Hg point-source precludes use of this core in evaluating historical trends in atmospheric Hg deposition.

Accumulation rates for Hg show a more consistent pattern among lakes within each region than do concentration profiles (Figs. 3–5). Hg accumulation rises above a stable preindustrial background sometime between 1860 and 1880 in virtually all lakes, although there is a hint of an earlier increase in the first half of the 19th century in some of the Northeast lakes (e.g., Wilson, Tooth [Fig. 4]). In essentially all of the Metro lakes there is a recent decline in Hg accumulation from peak values during the 1950s to 1970s (Fig. 3). The two Metro lakes without recent declines are perhaps understandable exceptions; Elmo was contaminated and Sweeney had dating problems (high and variable supported ^{210}Pb). In some Metro lakes the decline is parallel to a decrease in Hg concentration (e.g., Square, Harriet), suggesting a decline in atmospheric Hg inputs. But in many lakes the decline in Hg accumulation is linked to a drop in sediment flux, and Hg concentrations actually increase over the same time period (e.g., Gervais, Fish). This latter pattern suggests that Hg accumulation peaked because of inputs of soil-bound Hg from the catchment (a high flux of sediment with low Hg content) and the subsequent decrease in Hg accumulation was driven by a reduction in this load.

Hg accumulation profiles from the Northeast lakes are less irregular than those from the Metro lakes (Fig. 4). Cores from two subgroups (Grand Rapids and Voyageurs) show a consistent decline in Hg accumulation during the last 2–3 decades which coincides with decreasing Hg concentrations (e.g., Loon, Loiten). This reversal is not apparent in any of the other ten Northeastern lakes located in Lake and Cook counties (e.g., Wilson).

In the South Central group, the ten lakes with highly agriculturalized watersheds (e.g., Hook, Stahls, Dunns) show strong increases in Hg accumulation despite flat or declining Hg concentrations during the period of record (Fig. 5). There is a sharp decline in Hg accumulation around 1940 in the Diamond Lake core and smaller spikes in four other profiles that derive entirely from changes in sediment flux. Among the other five South Central lakes with smaller and less-developed catchments, four show a gradual rise in Hg accumulation similar to trends in the Northeast lakes (e.g., Kreighle), while Long Lake shows a reversal in both Hg flux and concentration after the 1970s.

Preindustrial Hg accumulation rates cover a narrow range and are remarkably similar among lake groups (Fig. 6A). Mean values are 10, 12, and $14 \mu\text{g m}^{-2} \text{ yr}^{-1}$ ($\text{SD} < \pm 7$) for Metro, Northeast, and South Central groups, respectively. This convergence of preindustrial Hg fluxes (in contrast to the regional divergence of modern fluxes) indicates that, prior to European settlement and industrialization, Minnesota lakes received similar loadings of Hg, and atmospheric deposition was the primary source. Preindustrial rates of atmospheric Hg deposition for the Midwest are estimated at about $3.7 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (Swain et al. 1992), which is lower than

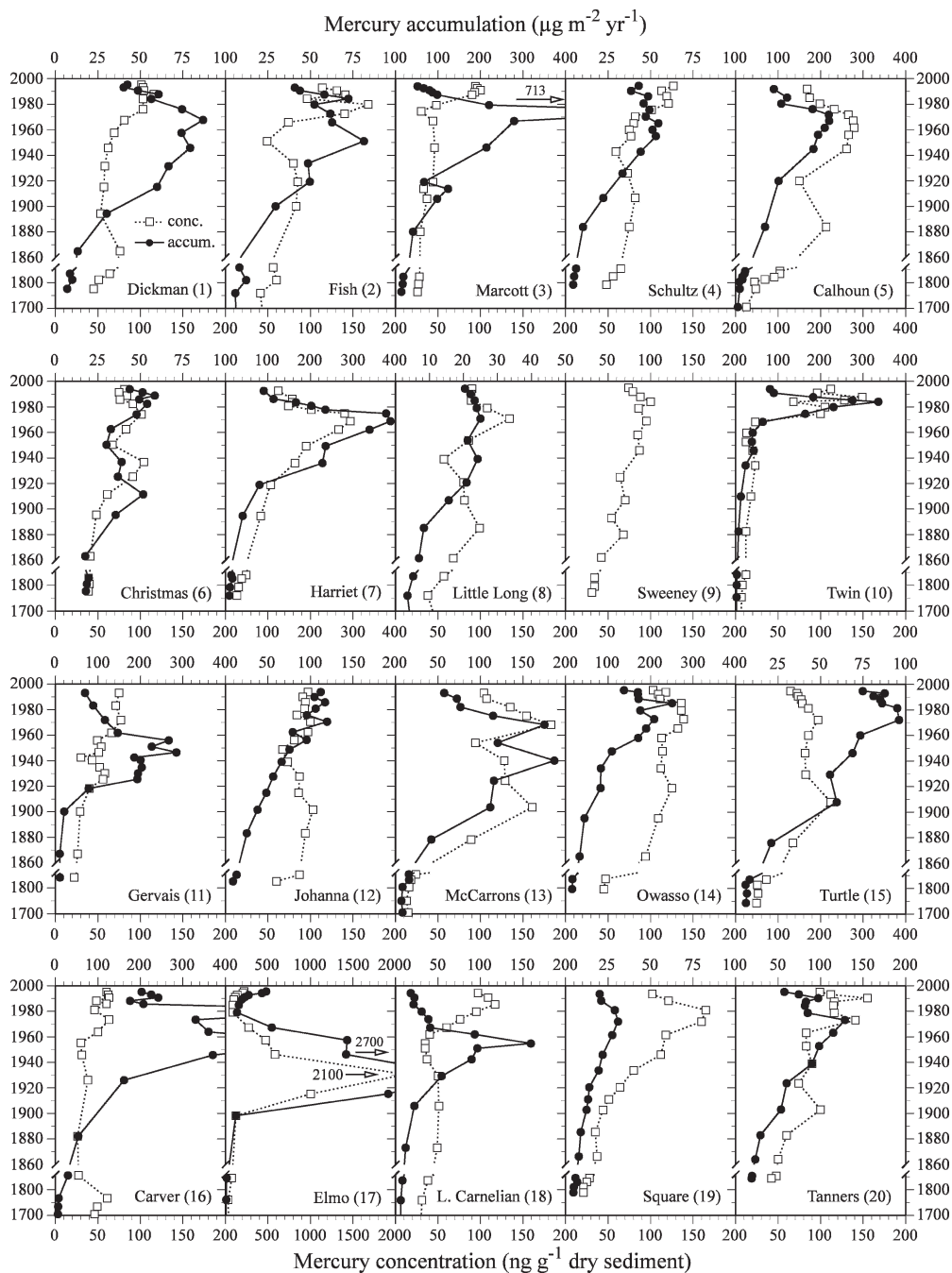


Fig. 3. Dated sediment profiles of Hg concentration and accumulation rates for study lakes from the Metro region of Minnesota, USA. No. following lake names refer to site identifiers in Fig. 1 and Table 1. Note differences in concentration and accumulation scales among lakes and age-scale break at 1850–1860.

most of the core-specific fluxes in this data set. However, lakes receive an additional load of atmospheric Hg from catchment runoff, and ^{210}Pb inventories (mean \pm 1 SD = 1.18 ± 0.47 Bq cm^{-2}) indicate at least modest sediment focusing in all lakes, which would also amplify the atmospheric signal in the sediment cores. Modern Hg fluxes (post-1994) are clearly elevated over preindustrial rates for all lake groups, although the increase is greatest for Metro and South Central lakes (means = 70 and 81 $\mu\text{g m}^{-2} \text{yr}^{-1}$, respectively) and smallest

for the Northeast group (mean = 39 $\mu\text{g m}^{-2} \text{yr}^{-1}$; Fig. 6C). The range of values within each lake group is also much greater (SD = 46, 22, 44 $\mu\text{g m}^{-2} \text{yr}^{-1}$ for Metro, Northeast, and South Central, respectively), which suggests that factors other than atmospheric Hg deposition are now influencing Hg loading to individual lakes—given our working hypothesis that atmospheric deposition is broadly uniform, especially within each of the three study regions. Ratios of modern to preindustrial Hg accumulation (Hg flux ratios) average 9.8

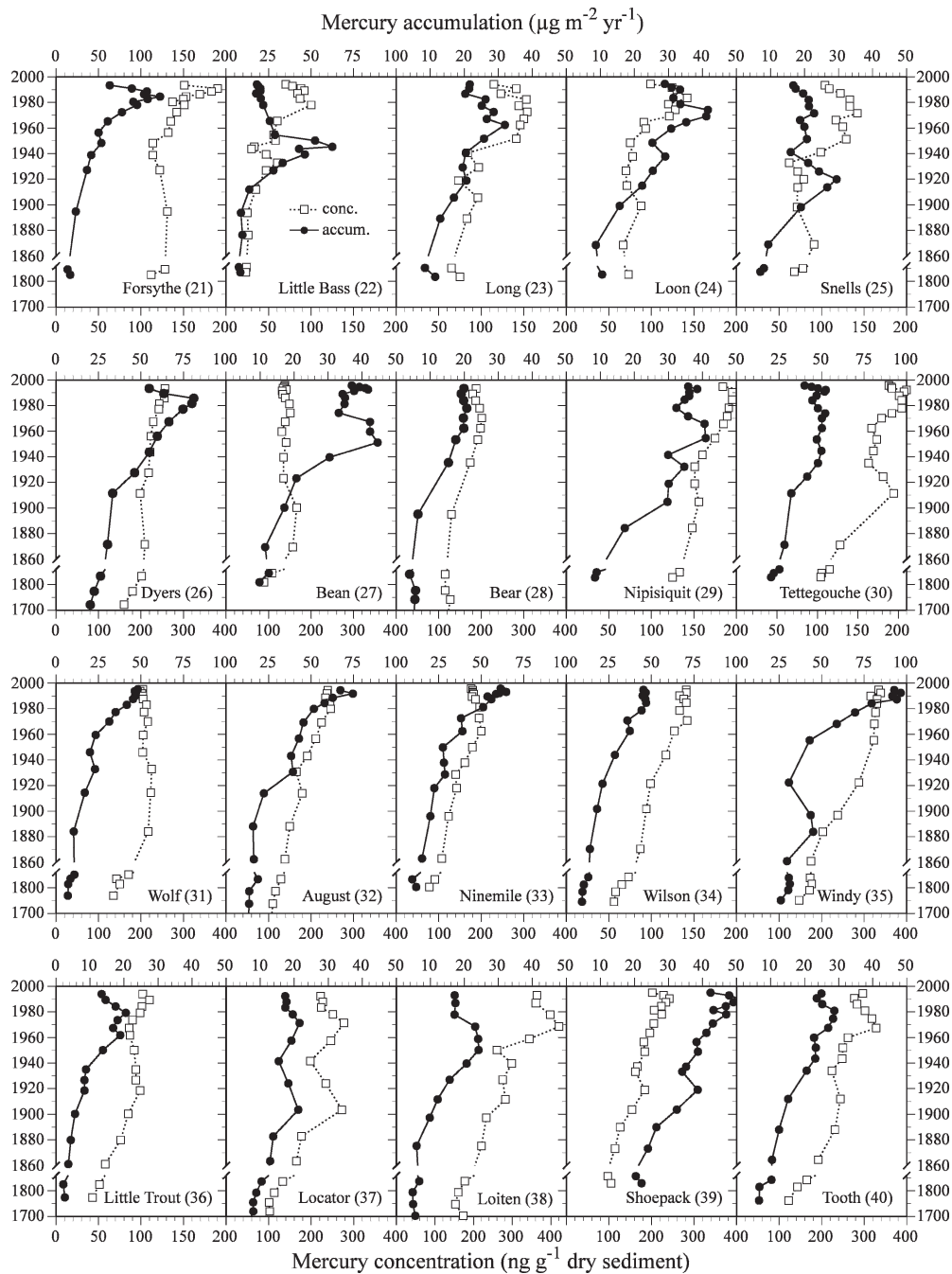


Fig. 4. Dated sediment profiles of Hg concentration and accumulation rates for study lakes from the Northeast region of Minnesota, USA. No. following lake names refer to site identifiers in Fig. 1 and Table 1. Lakes 21–25 are clustered in the Grand Rapids area, and lakes 36–40 are in Voyageurs National Park. Note differences in concentration and accumulation scales among lakes and age-scale break at 1850–1860.

(SD = 10.4) for the Metro lakes, 3.6 (SD = 1.4) for Northeast lakes, and 5.8 (SD = 2.3) for South Central lakes (Fig. 6D).

Discussion

Sediment records of Hg loading—A central assumption in our interpretation of these Hg sediment records is that they provide a reliable measure of Hg loading to the lakes—

from atmospheric deposition and watershed runoff—and that changes in these inputs will result in a proportional change in Hg accumulation in the sediments. There is a large body of experimental and observational evidence that this is so—that the records are stable over time and that external Hg loading is the dominant signal (Electric Power Research Institute [EPRI] 1996; Fitzgerald et al. 1998; Lindberg et al. 2007). However, other factors related

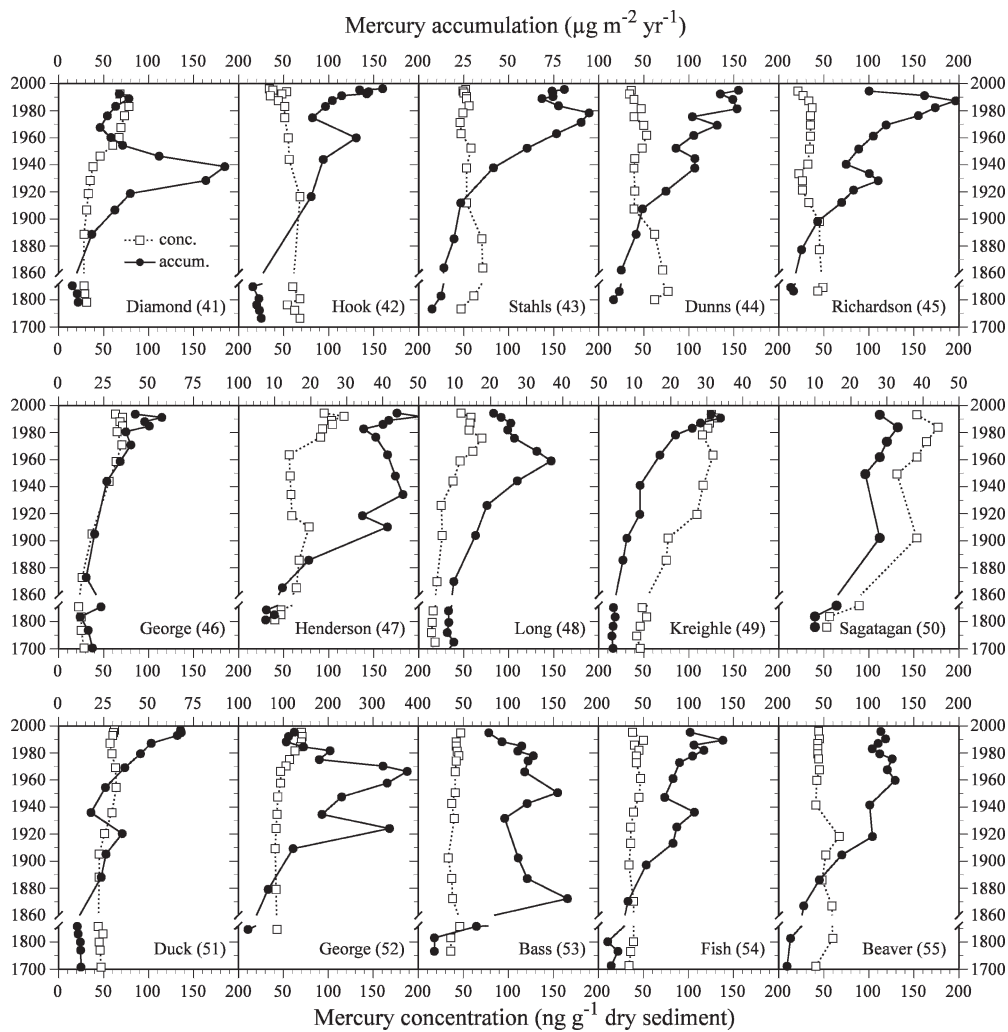


Fig. 5. Dated sediment profiles of Hg concentration and accumulation rates for study lakes from the South Central region of Minnesota, USA. No. following lake names refer to site identifiers in Fig. 1 and Table 1. Note differences in concentration and accumulation scales among lakes and age-scale break at 1850–1860.

to in-lake Hg cycling and sedimentation may influence the absolute rate of Hg accumulation in a core. A proportion of the incoming Hg may be lost to surface evasion or outflow, while the preferential deposition of fine-grained sediments in deeper parts of the lake (focusing) may magnify the actual rate of external Hg loading.

Because most lakes in this study have relatively small watersheds and long residence times (median = 3.2 yr), we would expect outflow losses of Hg to be small. Evasion, on the other hand, could be a significant flux and might vary among lakes depending on water chemistry and other factors. For example, evasion estimates for a geographically comparable set of Wisconsin lakes range from 7% to 51% of annual Hg deposition (Fitzgerald et al. 1991; Vandal et al. 1991; Watras et al. 1996), while whole-lake additions of stable ^{202}Hg in the METAALICUS experiment indicate evasion of about 45% of the isotopic spike (Southworth et al. 2007). Add to this the variability among cores caused by sediment focusing (a factor of two) (Engstrom et al. 1994), and the

comparability of Hg fluxes among sediment cores from 55 lakes might appear problematic.

However, there are clear trends and patterns within this large data set that are most readily explained by differences in external Hg loading. The patterns are apparent in the stratigraphic profiles of individual cores, among lakes within the same region, and within the entire 55-lake data set. This coherence coupled with the fact that the observed range in Hg flux is far too large (more than an order of magnitude) to be explained by in-lake processes alone, argues strongly that Hg loading is the primary driver. We recognize that differences (and changes) in lake chemistry, productivity, and hydrology almost certainly influence Hg sedimentation, but argue (below) that changes in Hg inputs to the lakes offers the most parsimonious explanation for the observed patterns.

Mercury and erosion—Results from this study show historical increases in Hg flux at all of the study sites, but the largest increases occur in the Metro and South Central

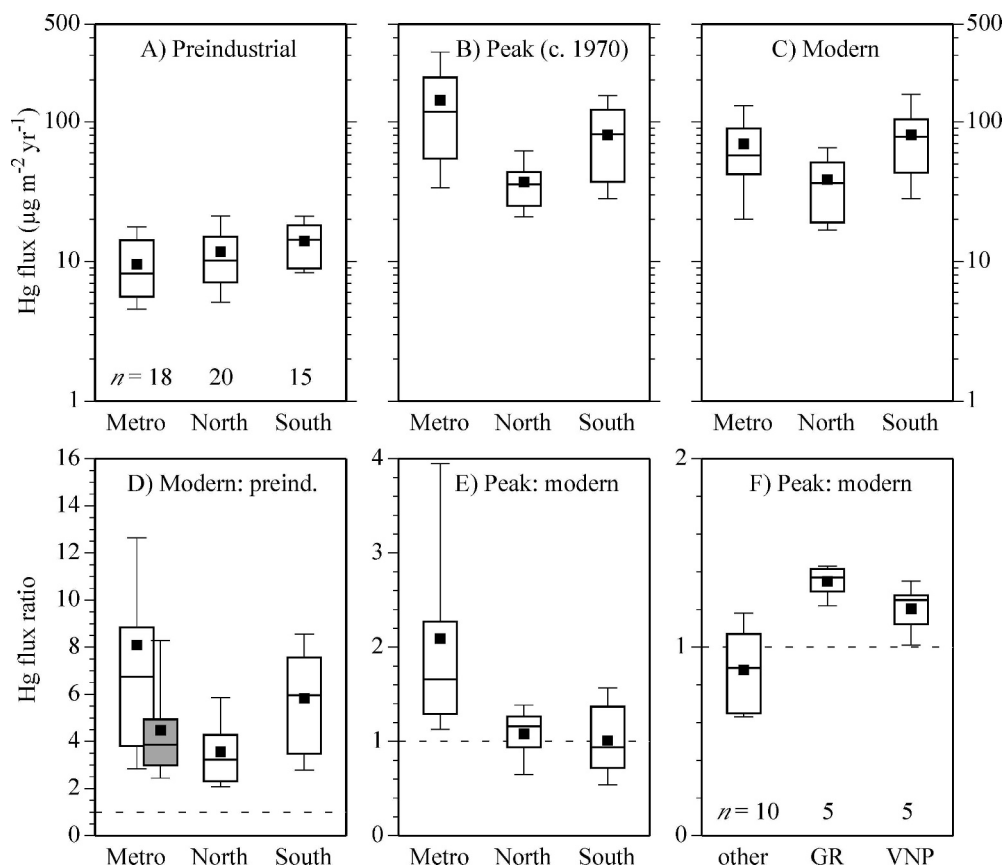


Fig. 6. Box plots of mean sediment Hg accumulation (flux) by region (A) prior to 1860 (preindustrial), (B) the interval of maximum Hg accumulation c. 1970 (peak), and (C) post-1994 (modern). Core intervals closest to 1970 were used for those profiles showing no clear Hg peak during the last four decades. Box plots of the ratio of Hg accumulation (flux ratios) for (D) modern: preindustrial; shaded box denotes a subset of 7 relatively undisturbed Metro lakes (see text), (E) peak: modern, and (F) peak: modern for the Northeast group only, broken into subgroups: GR = Grand Rapids, VNP = Voyageurs National Park, other = all other Northeast lakes. Dashed lines denote a flux ratio of 1 (no change). Box plots as described in Fig. 2.

lakes, and the smallest are in the Northeast group (Fig. 6D). Likewise, the increase in total sediment accumulation from preindustrial to modern times is highest in the South Central lakes and lowest in the Northeast (Fig. 2). The rise in sediment accumulation that follows European settlement at the Metro and South Central sites is typically accompanied by an increase in percent inorganic matter, which is composed primarily of detrital silicates from soil erosion (see Web Appendix 1). Because postsettlement land-use changes have been most severe in the Metro and South Central regions, these results strongly suggest a direct link between human disturbance in the watershed, increased erosion rates, and higher Hg loading to lakes.

A comparison of sediment geochemistry and accumulation rates for the entire 55-lake data set further illustrates the linkages between erosion rates and Hg flux. Present-day (post-1994) sediment accumulation (log-transformed) is strongly correlated with Hg accumulation ($r = 0.85$) but negatively so with Hg concentration ($r = -0.72$; Fig. 7). These relationships are somewhat weaker in preindustrial strata, especially that between sediment flux and Hg

accumulation rates ($r = 0.51$). The negative covariance between sediment flux and Hg concentration is also apparent within each of the three lake groups and in many of the Hg profiles from individual lakes where increasing sediment flux contributes to higher Hg accumulation and at the same time dilutes Hg concentration (e.g., Fish, Gervais, Dunns; Figs. 3, 5). The sediment source contributing to this change must, therefore, contain some Hg but less than that of the preexisting sediment matrix. Undisturbed forest soils in northern Minnesota have an A-horizon Hg content of 100–150 ng g⁻¹ (Nater and Grigal 1992), while agricultural soils in the southern part of the state have Hg concentrations of 25–50 ng g⁻¹ (S. J. Balogh, unpubl. data), very similar to concentrations on suspended sediment in the rivers draining this region (Balogh et al. 1997). These soil Hg levels are generally lower than that found in post-industrial sediments in this study, yet are sufficient to raise Hg loading to lakes if erosion rates were to increase. The surface soils are considerably enriched in Hg relative to underlying soil parent material, a build-up attributable to atmospheric Hg deposition (Nater and Grigal 1992; Grigal et al. 1994). The atmosphere is, thus, the ultimate source for

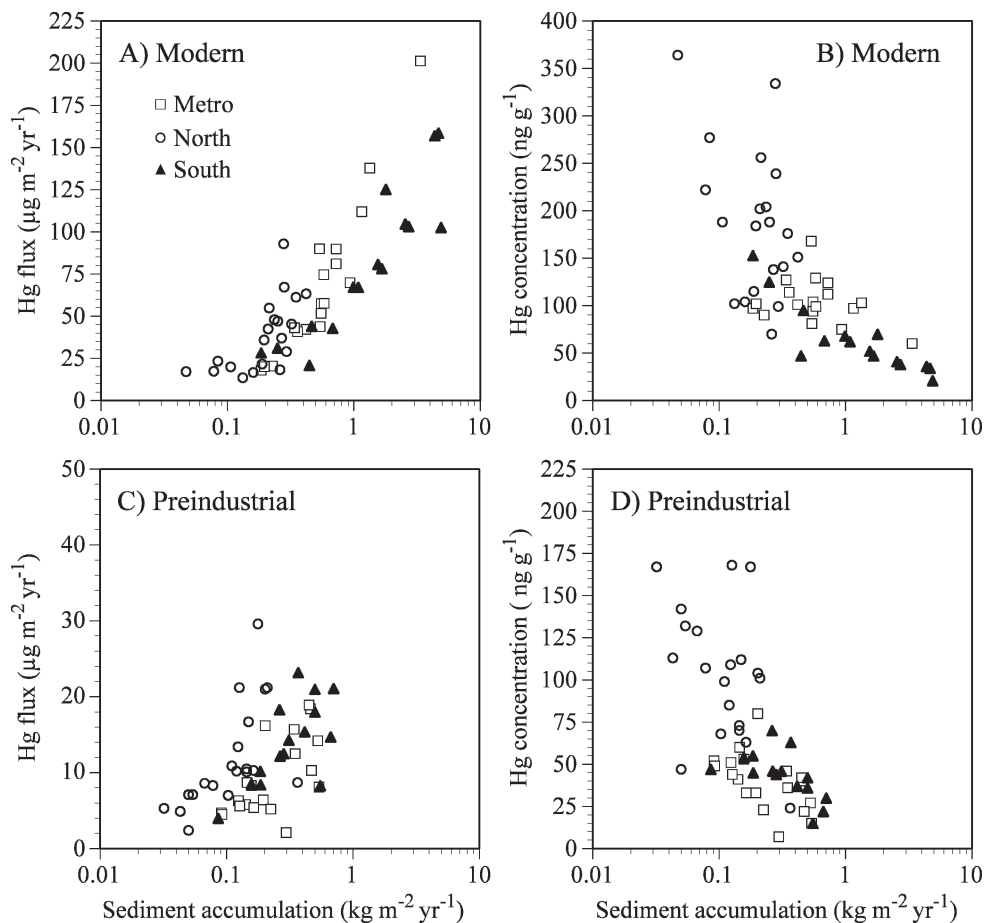


Fig. 7. Relationships between sediment accumulation and Hg concentration and accumulation among 55 study lakes for (A, B) modern (post-1994) and (C, D) preindustrial (pre-1860) periods.

most of the Hg entering Minnesota lakes, either from direct deposition to the lake surface or secondarily from catchment runoff and erosion.

The linkage between catchment land-use and Hg accumulation in lake sediments is clearly illustrated by a statistical comparison of GIS-based watershed parameters with modern (post-1994) Hg flux and total-Al accumulation (a proxy for detrital silicates; Table 2). Correlation matrices for the 55-lake data-set are split by region and exclude three problematic lakes from the Metro region: Elmo (local Hg contamination), Sweeney (undateable sediments), and Carver (extremely high sedimentation rates). Nonparametric tests (Spearman rank) yield similar results, indicating that the correlations are robust.

In the Metro lake group, correlations of Hg flux with cover-types for %Built-up and %Road are both highly significant ($r = 0.60$ and 0.58 , respectively, $p = 0.01$; Table 2). These results indicate that urban cover types (built-up and road) contribute more Hg to lakes than do rural cover types—Ag-land (agricultural) and Forest. The strong correlation between Hg and Al fluxes ($r = 0.76$) implies that Hg loading is enhanced by erosion. However, the correlations of Al flux with %Built-up ($r = 0.39$) and

%Road ($r = 0.21$) are relatively weak, suggesting that urbanized watersheds may contribute some excess Hg to lakes by means other than erosion (e.g., runoff from impervious surfaces such as roads via storm sewers that drain directly to a lake) or in association with particulate organic matter (Mason and Sullivan 1998) rather than clastic silicates. The strongly negative correlation of Hg flux with Slope is likely a surrogate relationship that arises because catchments with steep slopes are less built-up than those with more level terrain (the correlation between slope and %Built-up = -0.78). Likewise, the negative relationship between Hg flux and %Ag-land reflects the fact that percent cover-type is a closed data set, and catchments cannot simultaneously be built-up and agricultural.

For the South Central lakes, the strong correlations between Hg and Al fluxes ($r = 0.96$) and Hg and %Ag-land ($r = 0.72$; Table 2) implies that soil erosion contributes a substantial Hg load to lakes with highly agricultural catchments. Indeed, there is a clear separation in Hg flux among South Central sites; the subgroup of 10 lakes selected for their agriculturalized catchments ($>70\%$ Ag-land) has modern Hg accumulation rates in excess of $60 \mu\text{g m}^{-2} \text{yr}^{-1}$ (mean = $104 \mu\text{g m}^{-2} \text{yr}^{-1}$), while the other subgroup with more limited agriculture ($<40\%$ Ag-

Table 2. Correlations by region of present-day Hg fluxes in sediment cores with catchment land-use and other parameters; values in bold are significant at $p < 0.05$. Correlations are based on GIS data for the primary catchment, which excludes that portion of the watershed above the outflow from major upstream lakes. Results for the total catchment are similar. Data collected in Minnesota, USA.

	Metro	Northeast	South Central
C:L ratio*	-0.10	0.19	0.16
Slope†	-0.60	-0.14	-0.22
% built-up	0.60	0.13	-0.32
% ag-land	-0.55	-0.32	0.72
% forest	-0.49	0.01	-0.57
% wetland	-0.15	0.06	-0.40
% road	0.58	-0.05	-0.18
Al flux‡	0.76	0.69	0.96

* C:L = ratio of catchment area to lake-surface area.

† Slope = catchment mean slope class.

‡ Al flux, a proxy for silicate erosion, is the present-day flux of total-Al in the cores.

land) has Hg accumulation rates below $50 \mu\text{g m}^{-2} \text{yr}^{-1}$ (mean = $42 \mu\text{g m}^{-2} \text{yr}^{-1}$).

Hg flux and Al flux are also closely aligned in the Northeast data set, but none of the correlations with land use are statistically significant (Table 2). And contrary to initial expectations, the relationship between Hg flux and catchment:lake area ratio (C:L) was also very weak ($r = 0.19$). Swain et al. (1992) found that catchment:lake area ratio was a strong predictor of whole-basin Hg sedimentation in northeastern Minnesota lakes, but their Hg accumulation rates were based on multiple cores from each lake and, thus, corrected for spatial differences in sediment accumulation (focusing) within the lake basin. Sediment fluxes from individual cores can be normalized to the inventory of ^{210}Pb in the core—relative to the expected inventory from atmospheric ^{210}Pb deposition (0.6 Bq cm^{-2} ; Urban et al. 1990)—as a rough correction for sediment focusing, and this calculation does improve somewhat the fit between Hg flux and C:L ($r = 0.44$). Such results suggest that watershed characteristics in addition to catchment:lake area ratio may be important determinants of Hg flux to these relatively pristine lakes.

Results from the Metro and South Central lakes clearly show that urban and agricultural land-uses increase export of Hg from catchments to lakes and that soil erosion is the likely vector. Balogh et al. (1997, 1998) arrived at similar conclusions from their studies of Hg transport by tributaries of the upper Mississippi River in Minnesota. Annual Hg yields from the agriculturally dominated Minnesota River basin ($0.97\text{--}1.4 \text{ g km}^{-2}$; 1995–1996) were more than twice that of the Mississippi main stem ($0.46\text{--}0.51 \text{ g km}^{-2}$) or the St. Croix ($0.43\text{--}0.52 \text{ g km}^{-2}$) basins, both of which have much less agriculture than the Minnesota. Hg concentrations and loads in the Minnesota River were also closely tied to those of suspended sediment. Mason and Sullivan (1998) found even higher Hg yields from the urbanized Anacostia River ($11\text{--}30 \text{ g km}^{-2}$), a result that suggests both local Hg sources within the watershed and a substantial export of the atmospheric load.

The increase in Hg flux from preindustrial to modern times (M:P flux ratio) averages 9.8 for Metro region lakes and 5.8 for South Central lakes. M:P flux ratios from the Northeast sites range from 2.0 to 6.7 (mean = 3.6), which is more similar to that reported for other remote North American lakes with undisturbed catchments (Lucotte et al. 1995; Lockhart et al. 1998; Lorey and Driscoll 1999; Lamborg et al. 2002). Clearly, Hg inputs to many of the Metro and South Central lakes have increased well beyond that of lakes exposed solely to changes in atmospheric Hg deposition. Do these excess watershed loads result in a greater exposure of the biota to contamination by methyl mercury? As Hg levels in Minnesota's top predator fish species (walleye [*Sander vitreus*], northern pike [*Esox lucius*]) are highest in lakes in the northeastern part of the state (medians of 0.26 and 0.29 ppm, respectively) and significantly lower in lakes from elsewhere in the state (medians of 0.22 and 0.20 ppm) (MPCA 2007), it would seem that the answer is, no. It may be that particulate-bound Hg from soil erosion is unavailable for in-lake methylation, either because of low reactivity or rapid sediment burial (Hurley et al. 1998), or because Metro and South Central lakes are chemically predisposed to low rates of Hg methylation (high pH, high alkalinity, low DOC, low proportion of wetlands in the catchment) (Swain and Helwig 1989; Cope et al. 1990; Wiener et al. 2006).

Trends in atmospheric Hg deposition, modern: preindustrial increases—Increased Hg inputs to lakes may result from changes in atmospheric Hg deposition, land-use changes that alter Hg retention in the watershed, or both factors simultaneously. Contemporary Hg loading to lakes in southern Minnesota, both rural and urban, is significantly greater than that in the northern part of the state, and the question is whether this difference reflects higher rates of atmospheric deposition closer to Hg emission sources in the Minneapolis–St. Paul area or whether it is solely a function of land-use change, which is decidedly more pronounced in southern Minnesota.

The range of M:P flux ratios for lakes in the Metro and South Central regions are broadly similar, especially if two Metro outliers with ratios >30 , Twin and Carver, are discounted. Because these two regions differ greatly in their proximity to urban Hg emissions, one might conclude that increased soil erosion from land-use change—rather than near-source atmospheric deposition—was the primary cause of greater Hg loading to these lakes, as compared to those in the north. However, a more complicated pattern is revealed when Hg flux ratios are plotted relative to Hg concentration ratios for the three lake groups (Fig. 8A). Here the Northeast lakes form a cluster with low concentration- and low flux ratios; the South Central group has low concentration ratios, but tends toward higher flux ratios, and the Metro lakes have both high concentration- and high flux ratios. Within the Metro and South Central groups, the two ratios are negatively covariate, a pattern that results from soil erosion, which dilutes Hg concentrations but increases its flux. As discussed above, this pattern is evident in the stratigraphic profiles for individual lakes (Figs. 3–5) as well as in the

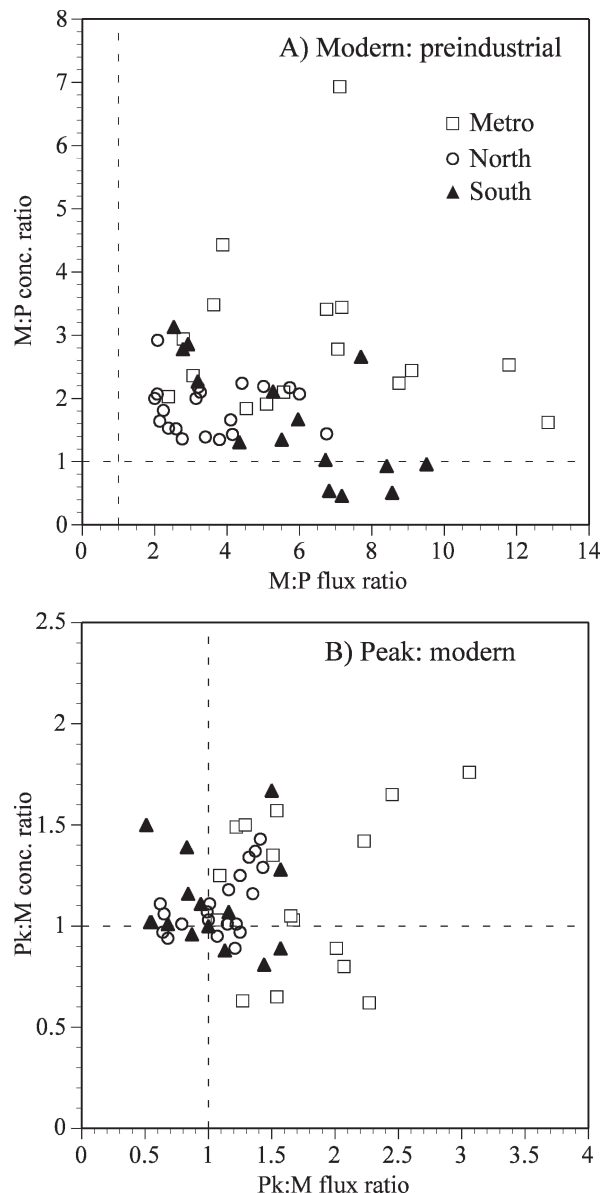


Fig. 8. Biplots of sediment Hg concentration ratios and flux ratios for the 55 study lakes for (A) M:P = modern : preindustrial ratios and (B) Pk:M = peak : modern ratios. Ratios as described in Fig. 6 and in the text. Two outliers with flux ratios >30, Twin and Carver lakes in the Metro group, are not shown.

distribution of Hg concentrations versus sediment accumulation (Fig. 7). Although there is some overlap among the three groups, the fact that most Metro lakes have higher concentration ratios (for any given flux ratio) suggests that Metro lakes are receiving additional inputs of Hg—either from atmospheric deposition or because of higher Hg concentrations on eroding particles—than remote Northeastern lakes or rural South Central lakes.

However, not all Metro lakes fall into this pattern. There is a group of six which clusters together with the Northeast group and those South Central lakes with low Hg flux ratios (Fig. 8A). This distribution is instructive, because five of these six lakes are located in rural areas at the farthest reaches of the Minneapolis–St. Paul metropolitan

area and have small, partially forested (>25%) catchments. Such lakes might be expected to receive lower Hg inputs, from both soil erosion and near-source atmospheric deposition. Indeed, if we take all seven Metro lakes that are both distant and minimally disturbed (Dickman, Marcott, Schultz, Christmas, Little Long, Little Carnelian, Square), the Hg flux ratios for this subset overlaps closely with the Northeastern group; the mean flux ratio is 4.5 (SD = 2.2) as compared to 3.6 (SD = 1.4) for the Northeast lakes (Fig. 6D).

These results suggest that lakes in the more urbanized core of Minneapolis–St. Paul presently receive additional Hg inputs from soil erosion as well as atmospheric deposition attributable to local emission sources. Additional evidence that present-day Hg deposition in the Minneapolis–St. Paul area is higher than that in out-state Minnesota comes from six years of precipitation sampling (1990–1995) summarized by Glass and Sorensen (1999). These results show higher fluxes of Hg in wet deposition near Minneapolis–St. Paul ($8.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ at Bethel and similar high number for 1994–1995 in Minneapolis) compared to more remote sites in the northeastern part of the state ($5.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ at both Ely and International Falls). However, such differences are small and may reflect differences in precipitation depth (1990–1995 mean of 85 cm yr^{-1} at Bethel compared to 65 cm yr^{-1} at the northeastern sites) as well as proximity to Hg emission sources in the urban region. Moreover, it is not clear from our sediment-core data whether present-day loads to Metro area lakes are higher because of contemporary Hg deposition, enhanced delivery due to impervious surfaces, or in-wash of soil-Hg that had been historically enriched by higher deposition rates from earlier decades. As argued below and in a previous paper (Engstrom and Swain 1997), atmospheric Hg deposition was substantially higher in the Minneapolis–St. Paul area during the 1960s and 70s, and local soils may, thus, contain a large burden of legacy mercury that could enhance contemporary Hg loading to Metro lakes and cause catchment Hg export to lag declines in atmospheric deposition by decades or longer. Similar conclusions regarding legacy Hg have been drawn for a suite of New England lakes by Kamman and Engstrom (2002).

Recent declines—A related question, also addressed in this study, is whether recent declines in Hg deposition reported previously for a small subset of Metro and Northeast lakes (Engstrom and Swain 1997) have occurred throughout Minnesota or are restricted to certain regions of the state. If the declines were widespread it would suggest that they resulted from emission reductions on a large regional scale, whereas more localized declines would point to reductions from local Hg sources.

Virtually all Metro lakes in this study show large and obvious declines in Hg flux over the last 2–3 decades. Peak Hg fluxes are typically observed between 1960 and 1980, and are on average about twice that of present-day (Fig. 6E). These results confirm earlier observations of historical declines in Hg flux to four Minneapolis lakes in which peak values during the 1960s and 1970s were 1.3–2.0 times modern (Engstrom and Swain 1997). Although some portion of this recent decline may be attributable to land-

use improvements that reduced soil erosion and associated export of Hg from catchment soils, over half of the Metro lakes also exhibit decreases in Hg concentration (Figs. 3–5 and 8B), a result that would not be expected if the only change was a reduction in soil erosion. Recall that erosion decreases Hg concentrations through dilution (while increasing Hg flux), so the most likely explanation for reduced Hg concentration and flux is a decrease in atmospheric Hg deposition to the Metro region.

The fact that Hg accumulation shows clear declines in virtually every lake, both proximal and distant from the city centers, provides strong evidence that Hg emissions from light industry, residential heating, waste incineration, and other diffuse sources have declined dramatically in recent years. That change combined with reductions in sediment loading (erosion) has cut Hg inputs to many of the lakes by more than half.

However, a different pattern emerges for nonurban areas of the state (Figs. 5, 8B). Among the 15 South Central lakes, only four show a post-1970s decrease in Hg flux (peak:modern flux ratio >1), and of these only two (Long, Richardson) show a simultaneous decline in Hg concentration. These results imply that if there was a decrease in Hg loading to lakes in this region, it was a consequence of land-use practices that reduced export of soil-bound Hg from local catchments. In northeastern Minnesota, about half of the lakes show recent declines in Hg flux, but in this case most of the same cores also show simultaneous decreases in Hg concentration (Figs. 4, 8B). The flux declines are not as large as those in the Metro region and are restricted to two regional clusters of lakes (Fig. 6F)—those located in Voyageurs National Park along the US–Canadian border (Little Trout, Locator, Loiten, Shoepack, Tooth), and another subset in the vicinity Grand Rapids, Minnesota (Forsythe, Little Bass, Long, Loon, Shells). For the Grand Rapids lakes, the ratio of peak:modern Hg flux averages 1.35 ± 0.08 (± 1 SD), while for the Voyageurs group the mean peak:modern flux ratio is 1.20 ± 0.13 . In the remaining 10 Northeastern lakes, Hg flux either increases continuously to the present or levels off in recent times.

These results suggest that Hg deposition has declined in the Grand Rapids and Voyageurs Park areas by 20–30% since the mid-1970s, but not appreciably so in other parts of northeastern Minnesota or in the south-central part of the state. Although these results are based on targeted lake clusters rather than a randomized design, it appears that these declines are local in nature as opposed to the regional–continental reductions that we envisioned in our earlier study (Engstrom and Swain 1997). Minnesota is at the low end of a Hg contamination gradient across the Great Lakes states (Nater and Grigal 1992), and the effect of continental Hg reductions may be discernible only closer to the majority of emission sources. On the other hand, there is some evidence that state-wide Hg deposition may have leveled off in recent years. Many of the Hg profiles from the South Central and Northeast regions flatten out or fluctuate irregularly during the last 2–3 decades, rather than increase monotonically (Figs. 4, 5). And it should be remembered that the response of Hg accumulation in lake sediments might be expected to lag modest emission reductions because of continued cycling of

the anthropogenic Hg burden in vegetation, soils, and wetlands within a local watershed.

If declining local Hg emissions are responsible for declining Hg deposition near Grand Rapids and Voyageurs National Park, the most likely sources that contributed to this trend are the paper mills in International Falls (Boise Cascade) and Grand Rapids (Blandin) and the large coal-fired boiler at Cohasset (Minnesota Power). Other potential emission sources, such as the taconite industry, are located equally close to lakes showing no Hg declines and do not have operational histories that could account for recent decreases in Hg accumulation (Berndt 2002).

Mercuric fungicides were widely used in the pulp and paper industry from the 1940s through the 1970s, and presumably much of this Hg ultimately volatilized to the atmosphere. Although records of Hg use by Minnesota paper mills are unavailable, on a nation-wide scale the combined application of mercuric fungicides for paper and agriculture peaked at 3.42×10^5 kg yr⁻¹ in 1954 and declined to near zero by 1980 (Engstrom and Swain 1997). At peak use, potential Hg emissions from fungicides exceeded that for coal combustion by an order of magnitude. The pulp and paper industry represents the one local Hg source that is unique to both Grand Rapids and Voyageurs Park.

Minnesota Power's Clay-Boswell plant at Cohasset, currently one of the state's largest Hg emitters, is located within 5 km of the Grand Rapids lakes, but it is unclear whether historical Hg emissions, especially those forms likely to deposit locally, follow the same time-trend as Hg accumulation in the sediments. Operational records extending back to the mid-1960s (T. Hagley, Minnesota Power, pers. comm.) show coal consumption rising stepwise from 0.4×10^9 kg in 1965 to about 3.5×10^9 kg in 1981 and leveling off thereafter. Based solely on coal consumption (assuming 0.05 mg Hg emitted per kg coal), potential Hg emissions remained relatively flat (~ 175 kg yr⁻¹) from 1981 until the cores were taken in the mid 1990s. However, controls on SO₂ and particulate emissions, a switch to western coal during the last two decades, and increased stack height may have encouraged long-distance Hg transport while reducing local deposition.

This evaluation of historical Hg accumulation in the sediments of 55 Minnesota lakes indicates that Hg loading was broadly similar across the state in preindustrial times. Prior to 1860, Hg accumulation rates in single cores from each lake ranged from 2–30 $\mu\text{g m}^{-2} \text{yr}^{-1}$ (median = 9 $\mu\text{g m}^{-2} \text{yr}^{-1}$) and showed little regional differentiation. Hg accumulation rates rose steadily following European settlement and regional industrial development, although sediment Hg concentrations were depressed in many Metro and South Central lakes by dilution from eroded soils due to agriculture and urbanization. Present-day Hg fluxes are significantly higher in the Metro and South Central regions (median = 58 and 78 $\mu\text{g m}^{-2} \text{yr}^{-1}$, respectively) than in the Northeast (median = 36 $\mu\text{g m}^{-2} \text{yr}^{-1}$), largely because of erosional inputs of soil-bound Hg from disturbed catchments. Higher rates of atmospheric Hg deposition are also indicated for the Metro lakes, although in-wash of “legacy”

Hg from historically enriched catchment soils is an equal possibility.

This analysis also supports previous observations that atmospheric Hg deposition in the Minneapolis–St. Paul area and certain parts of rural Minnesota has declined from peak rates in the 1960s and 1970s. The combined effects of atmospheric decreases coupled with reduced erosional inputs has cut Hg loading to many Metro lakes by more than half. Recent declines in Hg deposition to non-Metro study sites appear restricted to lakes in Voyageurs National Park and the Grand Rapids area. The localized nature of the declines implies a reduction in nearby Hg emissions, rather than the regional to continental-scale reductions suggested by earlier studies.

The collection, dating, and stratigraphic analysis of mercury for 55 lake cores was not a small task, nor one that would even be possible in areas lacking the abundant lakes that occur in Minnesota. However, the results demonstrate the empirical strength of regional comparisons to reveal the effects of both land-use change and anthropogenic Hg emissions on Hg loading to lakes. The core data also show a remarkable temporal concordance of Hg increases, despite an order-of-magnitude range in sediment accumulation rates among the lakes. As argued elsewhere (Fitzgerald et al. 1998), such uniformity is among the strongest evidence that lake-sediment cores preserve a conformable and reliable record of anthropogenic Hg contamination. That said, there are striking differences among lakes in the pattern and magnitude of Hg increase (and subsequent declines) which are only partially explicable in terms of Hg emission trends. Some of these differences are clearly due to local land-use changes that affect the export of Hg from catchment soils. However, even these environmental patterns would not be apparent or decipherable without a redundancy of data from multiple lakes and cores. Hg accumulation rates in lake sediments are subject to both uncertainty in sediment dating as well as natural variability in sediment deposition patterns and hydrologic factors that influence the retention and delivery of Hg to the lake itself. If there is a cautionary note here, it is that single cores from a small number of lakes can be easily misinterpreted with regard to trends in atmospheric Hg deposition. This is especially so for lakes with disturbed watersheds—virtually all lakes in urban and agricultural landscapes—where erosional inputs of Hg may overwhelm direct atmospheric deposition. And for lakes in regions with naturally low rates of atmospheric Hg deposition (e.g., the Arctic), catchment inputs pose an even larger problem for interpretation (Fitzgerald et al. 2005). Yet despite the problems of natural variability and multiple stressors, lake sediments remain our most powerful tool for understanding the magnitude and timing of human alteration of the global Hg cycle. Multiple cores and multiple lakes are required to make better sense of the patterns.

References

- ANDERSON, J. R., E. E. HARDY, J. T. ROACH, AND W. E. WITMER. 1976. A land use and land cover classification system for use with remote sensor data. U.S. Geological Survey Professional Paper 964.
- APPLEBY, P. G. 2001. Chronostratigraphic techniques in recent sediments, p. 171–203. *In* W. M. Last and J. P. Smol [eds.], *Tracking environmental change using lake sediments. Volume 1: Basin analysis, coring, and chronological techniques*. Kluwer Academic.
- BALOGH, S. J., M. L. MEYER, AND D. K. JOHNSON. 1997. Mercury and suspended sediment loadings in the lower Minnesota River. *Environ. Sci. Technol.* **31**: 198–202.
- , ———, AND ———. 1998. Transport of mercury in three contrasting river basins. *Environ. Sci. Technol.* **32**: 456–462.
- , Y. H. NOLLET, AND H. J. OFFERMAN. 2005. A comparison of total mercury and methylmercury export from various Minnesota watersheds. *Sci. Total Environ.* **340**: 261–270.
- BERNDT, M. E. 2002. Mercury distribution in the Biwabik Iron Formation and resulting emissions from Minnesota taconite companies. Minnesota Department of Natural Resources.
- BINDLER, R., I. RENBERG, P. G. APPLEBY, N. J. ANDERSON, AND N. L. ROSE. 2001. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: A coast to ice margin transect. *Environ. Sci. Technol.* **35**: 1736–1741.
- COPE, W. G., J. G. WIENER, AND R. G. RADA. 1990. Mercury accumulation in yellow perch in Wisconsin seepage lakes: Relation to lake characteristics. *Environ. Toxicol. Chem.* **9**: 931–940.
- EAKINS, J. D., AND R. T. MORRISON. 1978. A new procedure for the determination of lead-210 in lake and marine sediments. *International Journal of Applied Radiation and Isotopes* **29**: 531–536.
- ENGSTROM, D. R., AND E. B. SWAIN. 1997. Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* **31**: 960–967.
- , ———, T. A. HENNING, M. E. BRIGHAM, AND P. L. BREZONIK. 1994. Atmospheric mercury deposition to lakes and watersheds: A quantitative reconstruction from multiple sediment cores. p. 33–66. *In* L. A. Baker [ed.], *Environmental chemistry of lakes and reservoirs*. American Chemical Society.
- ELECTRIC POWER RESEARCH INSTITUTE. 1996. Protocol for estimating historic atmospheric mercury deposition EPRI/TR-106768. Electric Power Research Institute.
- FITZGERALD, W. F., D. R. ENGSTROM, C. H. LAMBORG, C.-M. TSENG, AND P. H. BALCOM. 2005. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. *Environ. Sci. Technol.* **39**: 557–568.
- , ———, R. P. MASON, AND E. A. NATER. 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **32**: 1–7.
- , 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.
- GLASS, G. E., AND J. A. SORENSEN. 1999. Six-year trend (1990–1995) of wet mercury deposition in the upper Midwest, U.S.A. *Environ. Sci. Technol.* **33**: 3303–3312.
- GRIGAL, D. F. 2002. Inputs and outputs of mercury from terrestrial watersheds: A review. *Environ. Rev.* **10**: 1–39.
- , E. A. NATER, AND P. S. HOMANN. 1994. Spatial distribution patterns of mercury in and east-central Minnesota landscape. p. 305–312. *In* C. J. Watras and J. W. Huckabee [eds.], *Mercury pollution: Integration and synthesis*. Lewis.
- HEIRI, O., A. F. LOTTER, AND G. LEMCKE. 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: Reproducibility and comparability of results. *J. Paleolimnol.* **25**: 101–110.

- HOYER, M., J. BURKE, AND G. KEELER. 1995. Atmospheric sources, transport and deposition of mercury in Michigan: Two years of event precipitation. *Water Air Soil Pollut.* **80**: 199–208.
- HURLEY, J. P., J. M. BENOIT, C. L. BABIARZ, M. M. SHAFER, A. W. ANDREN, J. R. SULLIVAN, R. HAMMOND, AND D. A. WEBB. 1995. Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environ. Sci. Technol.* **29**: 1867–1875.
- , S. E. COWELL, M. M. SHAFER, AND P. E. HUGHES. 1998. Partitioning and transport of total and methyl mercury in the lower Fox River, Wisconsin. *Environ. Sci. Technol.* **32**: 1424–1432.
- IVERFELDT, Å. 1991. Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water Air Soil Pollut.* **56**: 251–265.
- JACKSON, H. C. 1919. The effect of corrosive sublimate when used as a preservative in composite samples. *J. Dairy Sci.* **2**: 170.
- JOHANSSON, K. 1985. Mercury in sediment in Swedish forest lakes. *Verhandlungen der Internationalen Vereinigung für theoretische und angewandte Limnologie* **22**: 2359–2363.
- KAMMAN, N. C., AND D. R. ENGSTROM. 2002. Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from ^{210}Pb dated sediment cores. *Atmos. Environ.* **36**: 1599–1609.
- LAMBORG, C. H., W. F. FITZGERALD, A. W. H. DAMMAN, J. M. BENOIT, P. H. BALCOM, AND D. R. ENGSTROM. 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. *Global Biogeochemical Cycles* **16**: 1104, doi: 1110.1029/2001GB1847.
- LIANG, L., AND N. S. BLOOM. 1993. Determination of total mercury by single-stage gold amalgamation with cold vapour atomic spectrometric detection. *J. Anal. At. Spectrom.* **8**: 591–594.
- LINDBERG, S., AND OTHERS. 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **36**: 19–32.
- LOCKHART, AND OTHERS. 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry* **40**: 163–173.
- LOREY, P., AND C. T. DRISCOLL. 1999. Historical trends of mercury deposition in Adirondack lakes. *Environ. Sci. Technol.* **33**: 718–722.
- LUCOTTE, M., A. MUCCI, C. HILLAIRE-MARCEL, P. PICHET, AND A. GRONDIN. 1995. Anthropogenic mercury enrichment in remote lakes of northern Québec (Canada). *Water, Air, and Soil Pollution* **80**: 467–476.
- MASON, R. P., AND K. A. SULLIVAN. 1998. Mercury and methylmercury transport through an urban watershed. *Water Res.* **32**: 321–330.
- MINNESOTA POLLUTION CONTROL AGENCY. 2007. Minnesota statewide mercury total maximum daily load. March 27, 2007 final. Minnesota Pollution Control Agency.
- MUNTHE, J., AND OTHERS. 2007. Recovery of mercury-contaminated fisheries. *Ambio* **36**: 33–44.
- NATER, E. A., AND D. F. GRIGAL. 1992. Regional trends in mercury distribution across the Great Lakes states, north central USA. *Nature* **358**: 139–141.
- NEWLANDER, C. E. 1916. The Babcock Test: Notes on its use in determining the percentage of fat in whole milk, skim-milk, buttermilk, cream and whey. Bulletin No. 2. Michigan Agricultural College.
- SOUTHWORTH, G., AND OTHERS. 2007. Evasion of added isotopic mercury from a northern temperate lake. *Environ. Toxicol. Chem.* **26**: 53–60.
- STEINNES, E., AND E. M. ANDERSSON. 1991. Atmospheric deposition of mercury in Norway: Temporal and spatial trends. *Water Air Soil Pollut.* **56**: 391–404.
- SWAIN, E. B., D. R. ENGSTROM, M. E. BRIGHAM, T. A. HENNING, AND P. L. BREZONIK. 1992. Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* **257**: 784–787.
- , AND D. D. HELWIG. 1989. Mercury in fish from northeastern Minnesota lakes: Historical trends, environmental correlates, and potential sources. *Journal of the Minnesota Academy of Science* **55**: 103–109.
- URBAN, N. R., S. J. EISENREICH, D. F. GRIGAL, AND K. T. SCHURR. 1990. Mobility and diagenesis of Pb and ^{210}Pb in peat. *Geochimica et Cosmochimica Acta* **54**: 3329–3346.
- VANDAL, G. M., R. P. MASON, AND W. F. FITZGERALD. 1991. Cycling of volatile mercury in temperate lakes. *Water Air Soil Pollut.* **56**: 791–803.
- WATRAS, C. J., K. A. MORRISON, AND R. C. BACK. 1996. Mass balance studies of mercury and methyl mercury in small temperate/boreal lakes of the northern hemisphere. p. 329–358. *In* W. Baeyens [ed.], *Global regional mercury cycles sources, fluxes and mass balances*. Kluwer Academic.
- WIENER, J. G., AND OTHERS. 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. *Environ. Sci. Technol.* **20**: 6281–6286.
- WILLIE, S., AND S. BERMAN. 1995. NOAA/9—Ninth round intercomparison for trace metals in marine sediments and biological tissues. National Research Council of Canada, Institute for National Measurement Standards.
- WRIGHT, H. E., JR. 1991. Coring tips. *Journal of Paleolimnology* **6**: 37–49.

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