Trends in Atmospheric Mercury Deposition Across Minnesota: Evidence From Dated Sediment Cores From 50 Minnesota Lakes

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by

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TABLE OF CONTENTS

ABSTRACT

The objective of this study was to reconstruct from sediment cores the history of mercury inputs to 50 Minnesota lakes to determine: (1) whether lakes near Hg-emitting facilities receive significant local atmospheric deposition, (2) if erosion of soils from agriculture and urbanization contributes to greater loading of mercury to lakes, and (3) whether human activities have altered the rate at which these higher Hg loads are now being methylated. Trends in atmospheric deposition and watershed inputs were inferred from Hg accumulation rates in ^{210}Pb dated cores from 20 lakes in the Twin Cities metropolitan area, 10 lakes in west central Minnesota, and 20 lakes in northeastern Minnesota. The watershed of each lake was characterized by GIS analysis, and the proportion devoted to agriculture, forest, wetlands, and urban uses was calculated.

Results show that present-day Hg accumulation and Hg flux ratios (modern:preindustrial Hg accumulation) increase significantly with the percentage of watershed area under urban or agricultural land-use. Hg accumulation rates (both past and present) are strongly correlated with the flux of total-Al, a tracer for soil erosion. Present-day Hg accumulation rates are substantially higher in the Metro and West Central regions than in the Northeast, largely because of erosional inputs of soil-bound Hg from disturbed catchments. The additional load of Hg is primarily of atmospheric origin.

Present-day (about 1991-1996) Hg loading from direct atmospheric deposition, calculated by normalizing Hg-accumulation ratios to soil erosion, is about 35% greater today in the Twin Cites Metropolitan region than in rural areas of west central or northeastern Minnesota. There is no known single dominant source of mercury in the metropolitan area. Rather, the elevated loading is likely due to the aggregate of numerous sources, including coal combustion, sewage sludge incineration, solid waste incineration, and general volatilization from mercury releases.

Hg loading to Metro region lakes has declined by about 30% since the 1970s, apparently due to a combination of declining emissions and increased atmospheric transport away from the area. This decline coupled with reduced erosional inputs has cut Hg loading to many Metro lakes by more than half. Hg deposition has also declined in parts of northeastern Minnesota including Voyageurs National Park and the area around Grand Rapids. The decrease, representing 15-20% of peak Hg loading, is not evident in west central Minnesota or elsewhere in the Northeast. The localized nature of the decline implies a reduction in nearby Hg emissions (possibly the former use of mercuric fungicides by paper mills), rather than regional/continental-scale reductions.

The methylated portion of total-Hg (%MeHg) increases by a factor of 2-3 between 1940 and 1970 in 12 of 14 analyzed cores from northeastern Minnesota. This increase is thought to represent a historical change in Hg methylation that effectively multiplies the biological impact of increased Hg deposition. The relative increase in %MeHg in the 14 lakes is strongly correlated with water-chemistry variables that are commonly associated with elevated MeHg levels in fish (low pH and ANC, high DOC and apparent color). Increased deposition of other atmospheric contaminants, particularly sulfate and nitrate, is the most likely cause for enhanced methylation in these remote lakes.

INTRODUCTION

One of the central questions surrounding atmospheric mercury pollution is the relationship between mercury (Hg) emission sources and the deposition that occurs at a given location (EPRI, 1996). In Minnesota and elsewhere we currently do not know how much deposition results from local emissions and how much comes from long-distance transport from regional and global sources. In previous studies funded by the Legislative Commission on Minnesota Resources (LCMR) we learned that Hg deposition in out-state Minnesota is elevated three-fold over natural (preindustrial levels) and that in pristine (forested and undeveloped) watersheds, about 20% of incoming Hg is washed into lakes; the remainder is retained in the soils or re-emitted to the atmosphere (Swain *et al*., 1992; Engstrom *et al*., 1994). More recently our studies of the Minneapolis chain of lakes show that peak Hg inputs to these sites were elevated 9-16 times above background (preindustrial) levels -- well above the increase in out-state Minnesota (Engstrom & Swain, 1997). These results suggest that Hg deposition in the Twin Cities 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.

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 dated sediment cores from 20 lakes in the Twin Cities metropolitan area, 10 lakes in the agricultural parts of west 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 impacts.

The first of three major questions addressed in this research is whether watershed disturbance might increase the export of Hg from catchment soils to downstream aquatic environments. Both sediment-core studies and watershed budgets for Hg indicate that upwards of 80-90% of atmospherically deposited Hg is retained in the soils of undisturbed forested catchments (Mierle, 1990; Engstrom *et al*., 1994; Hultberg *et al*., 1995; Lorey & Driscoll, 1999). Although a large portion of this load is ultimately revolatilized back to the atmosphere as Hg°, both the inventory and concentration of Hg in surface soils is relatively high (Nater & Grigal, 1992; Grigal *et al*., 1994). Thus is seems likely that land-use changes that might increase rates of soil erosion could also enhance the flux of Hg to lakes. Indeed, recent mass-balance studies suggest that Hg yields from urban and agricultural watersheds may greatly exceed those from forested catchments (Balogh *et al*., 1997; Balogh *et al*., 1998; Mason & Sullivan, 1998). Moreover, much of the Hg transported from these disturbed watersheds moves during storm events and is associated with high loads of suspended sediment.

The second question that this research attempts to answer is 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 & Andersson, 1991; Nater & Grigal, 1992; Landers *et al*., 1998) show clear spatial gradients of higher Hg loading near Hg emission sources in industrialized areas of North America and Europe. It is reasonable to ask whether such 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.

Although the Minneapolis-St. Paul metropolitan area 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, 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.

The third and final question addressed in this study is whether the accumulation of total Hg (Hg_T) in the sediments accurately records exposure of Minnesota lakes to methyl mercury (MeHg) or whether human activities have altered rates of MeHg production within lakes or their catchments. The production of methyl mercury (MeHg) is the critical process controlling Hg bioaccumulation in aquatic systems, but because MeHg represents just a small fraction of the Hg_T load to a lake, slight changes in methylation (or demethylation) could have major consequences for human and wildlife exposure to MeHg that are independent of the flux of Hg_T. Recent experimental studies suggest that Hg methylation by sulfate reducing bacteria may be enhanced in some lakes and wetlands by atmospheric deposition of sulfate (Gilmour *et al*., 1992; Gilmour *et al*., 1998). There is also limited evidence that MeHg is preserved in lake sediments in proportion to its net production within the lake and its watershed. Sediment profiles may thus provide a historic account of both inorganic and biologically active mercury species. Fifteen cores in this study were analyzed for MeHg as well as Hg_T to determine whether MeHg accumulation has kept apace with the flux of Hg_T or whether it has increased even more so because of historical increases in net methylation rates.

METHODS

Site Selection

Study lakes were selected from each region 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 west 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 (see below).

Core Collection

A piston corer equipped with a 7-cm diameter polycarbonate core barrel and operated from the lake surface by Mg/Zr alloy drive-rods was used to collect a continuous 1-2 m section of the upper sediments at all coring sites (Wright, 1991). This device recovers the watery, uncompacted sediment surface as well as deeper strata without disturbance or displacement (core-shortening) (Blomqvist, 1985; Blomqvist, 1991). 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. Differential GPS was used to record the location of core sites.

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 (Dean, 1974). Sediment samples of 1-2 g were dried overnight at 100° C and ignited at

550° and 1000° C for 1 hr 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 preindustrial 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 for the past 150-200 years. 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 - 7.0 g dry sediment at 550° C following pretreatment with concentrated HCl and plated directly onto silver planchets from a 0.5 N HCl solution (Eakins & Morrison, 1978). Activity was measured for 1-3 x 10^5 s with ion-implanted or Si-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 (Appleby & Oldfield, 1978) with confidence intervals calculated by first-order error analysis of counting uncertainty (Binford, 1990).

Mercury Analytical

Total Hg was determined in freeze-dried sediment samples from each core. Subsamples (0.1 g) were digested in 10 mL HNO_3:H_2SO_4 (70:30 v:v) at 65° C for 4 hrs in rigorously acid-leached 60-mL Teflon vials. Samples were cooled, then 6 mL $KMnO_4$ (5% w/v) and 3 mL $K_2S_2O_8$ (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 & 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 (n=56; relative standard deviation (RSD)=9%; certified value=1030 ng/g). The mean concentration of Hg in BCSS-1 was determined to be 170 ng/g (n=50; RSD=4%; accepted value=176 ng/g (Willie & Berman, 1995)). 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 (3 times the standard deviation of our reagent blank determinations (n=55)).

Methylmercury (MeHg) was determined in freeze-dried sediment samples from 15 cores and all core-top samples. Subsamples (0.2 g) were extracted in 2 mL 18% (w/v) KBr + 5% (v/v) H_2SO_4 and 0.4 mL 1 M $CuSO_4$ under gentle shaking for 1 hr (Bloom *et al*., 1997). MeHg in the sediment slurry was transferred into 10 mL CH_2Cl_2 under vigorous shaking for 1 hr. The organic phase was separated, and MeHg was back-extracted into 75 mL distilled deionized water by boiling at 50 °C. The aqueous phase was purged with N_2 for 15 min to remove all traces of CH_2Cl_2. MeHg was determined by aqueous phase ethylation with Tenax preconcentration/gas chromatography/atomic fluorescence detection (Bloom, 1989; Liang *et al*., 1994). The mean relative standard error for 18 duplicate analyses was 15%. The mean MeHg concentration determined in the certified estuarine sediment BCR-580 was 53.1 ng/g (n=22; RSD=16%; certified value=75.5 ng/g). Our method detection limit, calculated as 3 times the standard deviation of our reagent blank determinations (n=19), was 0.02 ng/g.

GIS Database

The Hg/GIS database contains seven thematic layers in Arc/Info format for each of the 50 watersheds. Each layer is cast in the Universal Transverse Mercator (UTM) Zone 15 projection with units in meters, the North American Datum (NAD) 1983 for horizontal reference, and the Global Reference System 1980 (GRS80) as the selected spheroid. The seven themes and their descriptions are as follows:

Theme	Description
Basemap	a template containing watershed boundary polygon(s) to which all other covers in the watershed database are registered.
Transportation	a derived arc layer containing eight feature classes: city streets, county roads, county state-aid highways, township roads, ramps and loops for trunk highways, trunk highway system, railroads, and runways.
Land Cover	a polygon cover consisting of ten feature classes: grassland, agland, brushland, deciduous forest, conifer forest, mixed forest, open water, wetlands, built-up, and clear-cut.
Streams	a derived arc layer containing three stream feature classes: perennial streams, intermittent streams, and manmade drainage ditches.
Core and Pour Points	a point cover containing the GPS location of the lake core sample and pour points representing the locations on the watershed boundary that separates an upstream feeder watershed from the downstream study watershed and/or outlet of the study lake watershed.
Slope	consists of polygons each having a slope attribute of one of six possible slope ranges calculated as a percent.
Aspect	consists of polygons each having an aspect value of one of nine possible aspect ranges.

Watershed boundaries where initially delineated on USGS 7.5-minute series topographic quadrangles for each of the study lakes and for any upstream basins. Basin boundaries where quality checked and reviewed for positional accuracy before being transferred to dimensionally stable Mylar. These delineations where digitized in ArcEdit to form the Basemap cover. As a final check, the location of the digital basin boundaries where fine-tuned against elevation values from U.S. Geological Survey (USGS) 30 meter Digital Elevation Models (DEMs).

The source data for the Transportation and Streams covers is the State of Minnesota BaseMap developed by the Minnesota Department of Transportation (MNDOT). In BaseMap, each of the transportation and stream classes occur as separate thematic covers. A series of spatial overlays of the BaseMap covers generated two derived covers that contain the combined classes of the desired transportation and stream covers. Finally, the transportation and stream features where clipped from the two derived covers using the watershed polygons in the Hg/GIS Basemap cover.

Slope and Aspect covers where initially created in Arc/Info GRID and then converted to polygons. Source data are the USGS 30 meter DEMs. Slope values assigned to each 30 meter cell where calculated as a percent and then grouped into ranges that correspond to common slope values found in soil surveys. For example, all cells having a calculated

slope within the range 0 to 2 % where grouped into polygons and given an attribute code of 1. Likewise, cell aspect values where also assigned to nine aspect range codes and grouped into polygons. Aspect codes vary from 1 to 8 for cells that have calculated aspects of 22.5 degrees on either side of major compass headings, i.e., code 1 = North (all cells with an aspect value of 337.5 to 22.49 degrees), code 2 = Northeast (all cells with an aspect value of 22.5 to 67.49 degrees), etc., and an additional code of -1 assigned to flat regions.

The Core and Pour Point theme is a point cover. Source data include the GPS coordinates for sediment-core locations. Pour points where digitized in ArcEdit from locations identified on the basin boundary delineation. Additional attributes where added to these features including the common lake name and the Minnesota Department of Natural Resources lake number.

The Land Cover layer contains polygons representing ten landscape features based on a modified USGS classification scheme (Anderson *et al*., 1976). These features where interpreted from early Spring 1991/92 Color Infrared (CIR) National Aerial Photography Program (NAPP) photographs. Stereoscopic interpretations where accomplished using an Old Delft Scanning Stereoscope with a 4.5 magnification setting resulting in an image scale of about 1:9000. Landscape feature delineations where recorded on a dimensionally stable acetate overlay. The combined photo/acetate with interpretations is the manuscript used for digital data development.

Landscape feature classes where digitized using ArcEdit and a USGS Panchromatic Digital Orthophoto Quarter Quad (DOQQ) as a background image. The manuscripts created above where used as a digitizing guide for this heads-up method. This procedure works well because the interpreted landscape features are easily identifiable in the high resolution black and white background image. Using the DOQQs as a background image for digitizing also eliminates feature displacement errors caused by camera tilt and terrain relief. Approximately 50% of the watersheds in the study where spot field checked for classification accuracy.

RESULTS

Study Sites

Location:

The 50 study sites were selected from three broad geographic regions of Minnesota (Fig. 1, Table 1). Twenty of the lakes are located within the greater metropolitan area of Minneapolis and St. Paul, with four in Dakota County, six in Hennepin County, and five each in Ramsey and Washington counties. Roughly half of the lakes in this "Metro" group are imbedded 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 (Fig 1). Five of these "Northeast" lakes are tightly clustered near the city of Grand Rapids in Itasca County, within a radius of 15 km of Minnesota Power's coal-fire boiler at the town of Cohasset. Another five of the Northeast lakes are located within Voyageurs National Park near the U.S./Canadian border in St. Louis County. The large Boise Cascade pulp mills and the city of International Falls are located 30-70 km to the northwest of these sites. Another six of the Northeast lakes are situated within the Lake Superior highlands of southern Lake and Cook counties. The lakes in this subgroup occur within 5 km of the North Shore of Lake Superior and are less than 11 km from

small coal-fired (taconite-industry) boilers at Silver Bay (5 lakes) and Taconite Harbor (1 lake). The remaining four Northeast lakes are located within the Superior National Forest in central Lake County. The Northeast group of lakes are among the most pristine in the 50-lakes data set and have little or no human development within their watersheds (see GIS results).

A third group of 10 lakes is situated within the largely agricultural landscape of west central Minnesota (Fig 1). Four of the lakes are in Kandiyohi County and two each are in Stearns, Meeker, and Mcleod counties. Half of these "West Central" lakes have relatively large, agriculturally dominated watersheds and are of poor water quality, while the other half have small watersheds, high water quality, and less agricultural influence (see Water Chemistry results). All of the lakes are rural, and many are ringed with summer cottages and lake homes (see GIS results).

Geology and Climate:

The Northeast lakes, with the exception of those in the Grand Rapids area, are underlain by Precambrian crystalline bedrock and a thin veneer of non-calcareous glacial drift of the Superior and Rainy ice lobes. In contrast, the Metro and West Central lakes are situated in thick carbonate-rich drift derived from Cretaceous and Tertiary sedimentary rocks by Demoine lobe ice from the northwest. The Grand Rapids lake basins are more akin to those in the Metro and West Central regions, as this part of northeast Minnesota was overridden by a sublobe of Demoine ice near the end of the Wisconsin glaciation (Wright, 1972).

The study lakes span a climatic gradient that becomes appreciably drier toward the southwest. Mean annual precipitation ranges from 70-75 cm in northeastern Minnesota and the Metro area to 60 cm in the west central region; evaporative losses exceed precipitation in the west and represent about 70% of the precipitation falling in the Northeast. Precipitation chemistry varies along the same gradient with pH increasing from 5.0 in northeastern Minnesota (Ely) to 5.4 in southwestern Minnesota (Lamberton). The corresponding values for wet sulfate deposition range from 5.3 kg ha^{-1} yr^{-1} in northeastern Minnesota to 7.8 kg ha^{-1} yr^{-1} in the southwestern Minnesota (averages for 1990-96) (NADP/NTN, 1997). These chemistry trends are driven largely by higher deposition of sulfate and carbonates in agricultural dust in the southwestern part of the state.

Physical Setting:

The study lakes range in size from 5.3 to 644.8 ha, although only two of the lakes (Diamond and Wilson) exceed 200 ha (Table 1). The range of lake surface areas is similar for the Metro and Northeast groups (median area = 38 and 47 ha, respectively) and only slightly larger for the West Central group (median = 76 ha) (Fig 2). Maximum lake depth for the entire data set ranges from 2.4 to 42.7 m, and the distribution of depths is broadly similar among the three regions (median = 13.1, 10.5, and 11.4 m, respectively for Metro, Northeast, and West Central groups) (Fig. 2).

Total catchment area (excluding lake surface) for the 50 study sites ranges from 32 to 4028 ha (Table 1), with catchments in the Northeast group being somewhat smaller and more tightly grouped (median = 265 ha, interquartile range IQR = 641 ha) than those in the Metro area (median = 418 ha, IQR = 1082 ha) or West Central region (median = 492 ha, IQR = 1066 ha) (Fig. 2). The ratio of total-catchment to lake-surface area for the entire data set ranges from 1.12 to 120.8 with a median value of 6.31 and an IQR of 12.13.

About half of the 50 lakes receive drainage from upstream lakes within their catchments. The primary catchment, which excludes that portion of the watershed above the outflow from these lakes, ranges from 18 to 1850 ha and in most cases is less than half that of the total catchment (Table 1). The ratio of primary-catchment to lake-surface area is thus smaller and covers a narrower range (median = 3.15, IQR = 4.49) than the same ratio calculated for the total catchment.

The catchments in northeastern Minnesota are topographically steeper (median value for mean slope class = 2.78) than those in the metro region (median = 2.04) and even more so than those in west central Minnesota (median = 1.85), although there is broad overlap among regions (Fig. 2).

Land-use:

The most striking difference among the three lake groups is in catchment land-use cover. The catchments of the Metro lakes are dominated by built-up cover types (residential and commercial), those in the Northeast by forest (conifer and deciduous), and catchments in the West Central group by agriculture (pasture and tillage) (Fig. 2). Moreover, there is little overlap among groups. The median for built-up in Metro catchments is 76%, with only two lakes (Schultz and Little Long) having less than 20% in this cover type (Table 2). By contrast, no Northeast lakes and only two West Central lakes (George and Henderson) have more than 10% built-up cover (lake-shore homes) in their catchments.

Among the West Central lakes, five catchments exceed 50% agricultural land-use and four others have more than 20% of this cover (Table 2). In the Metro area, only three lakes (Elmo, Little Carnelian, and Square -- all in Washington County) have greater than 20% of their catchments in agriculture, although most lands in the Metro region were intensively farmed at one time. Among the Northeast group, only those lakes in Itasca County (the Grand Rapids subgroup) have any agricultural land in their catchments, and only one (Snells) has greater than 20% in this cover type.

Fourteen of the Northeast lakes have catchments that are entirely undeveloped (forest or wetland), and five more are more than 80% undeveloped, while only three Metro lakes (Schultz, Little Long and Twin) and two West Central lakes (Kreighle and Sagatagan) have more than 50% of forest or wetland in their catchments (Table 2). Although land-use cover was an important criterion in lake selection, and the resulting contrast among the three lake groups was in effect pre-determined, the distribution of cover types for the 50-lake data set is highly representative of the larger population of lakes within each of the regions.

Water Quality:

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. The Northeast lakes, which lie mostly in thin, non-carbonate drift and crystalline bedrock, are characterized by low alkalinity (median = 0.34 meq/L, IQR = 0.44 meq/L) and circumneutral pH (median = 7.4, IQR = 0.7) (Fig. 2). Were it not for the Grand Rapids subgroup of Northeast lakes, which are located in calcareous drift and have (except for Forsythe) alkalinities around 2.5 meq/L and pH > 8.0, there would be no overlap in major ion chemistry with the Metro or West Central groups (Table 3). Lakes in these latter two regions have a median pH of 8.5 and alkalinities in excess of 1.5 meq/L. Median alkalinity in the West Central group (3.05 meq/L) is considerably higher than that of Metro group (2.17 meq/L), due in part to longer residence time (greater evaporation) and higher carbonate content of the glacial drift in Western Minnesota (Gorham *et al*., 1983).

The three lake groups also differ with respect to trophic conditions, with the Northeast group characterized by low total-P (median = 13 μg/L, IQR = 5 μg/L) and chlorophyll-a (median = 2.9 μg/L, IQR = 1.9 μg/L) and high Secchi depth transparency (median = 2.9 m, IQR = 2.2 m) (Fig. 2). Although several Metro area lakes (Christmas, Little Long, Square, Little Carnelian) and two in West Central Minnesota (George and Kreighle) have similarly high water quality, the other lakes in these two groups would be classified as mesotrophic to eutrophic based on total-P and related indices (Table 3). The median value for total-P for the Metro group is 24 μg/L, and that for the West Central group is even higher (38 μg/L). The major determinant of trophic condition is clearly land-use; lakes in largely forested catchments with limited agriculture or built-up cover types have lower total-P, chl-a, and higher Secchi depths. Lakes with very small surficial watersheds also tend to have higher water quality, even in cases where there is substantial lake-shore development or agricultural land-use (e.g. George and Christmas lakes).

Other water-quality parameters break down less clearly by geographic region. Dissolved organic carbon (DOC) levels are somewhat lower in the Metro lakes than in the other two groups; at least there are few values in excess of 8 mg/L in Metro lakes, which is near the median for the Northeast and West Central groups (Fig. 2). Sulfate concentrations are generally lower in northeastern Minnesota than elsewhere in the State, which again reflects the low sulfur content of the local geology (Table 3).

Sediment Cores

Field Descriptions:

The collected sediment cores ranged in length from 0.8 to 2.0 meters, and in all cases extended well into older strata of preindustrial age (see ^{210}Pb dating). The sediment/water interface was always recovered intact and core lengthening caused by gas expansion following retrieval was minimal (usually zero and never more than 5% of the *in situ* length). Sediment composition in Northeast lakes ranged from a cohesive brown gyttja to a fine-grained dy. The upper strata were typically very watery (93-98% water), but aside from a gradual increase in solids down core, there were no obvious changes in sediment lithology with depth. In contrast, cores from the Metro and West 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. The upper sediments were always fine-grained, but those at depth frequently contained coarser plant fragments within the fine-grained matrix. This lithologic transition, which was almost always accompanied by a change in loss-on-ignition 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.

Loss on Ignition:

Stratigraphic profiles of organic, carbonate, and inorganic content in sediment cores from the 50 study lakes show several distinctive patterns that reflect both local geology and the history of human impact within the catchment. Geological influence is clearly manifest in the low concentrations of sedimentary carbonate and the correspondingly higher values for organic and inorganic matter in cores from the Northeast lakes as compared to the Metro or West Central lakes (Fig. 3). The median carbonate content for preindustrial sediments (pre-1860 average) in Northeast lakes is less than 5%, whereas the preindustrial median for Metro and North Central lakes is 13% and 18%, respectively. The Northeast group (except for the Grand Rapids subgroup), is comprised of low alkalinity Canadian Shield lakes that are too dilute to precipitate calcium carbonate. The

West Central lakes, on the other hand, have the highest alkalinities in the data set (Fig. 2), and their sediments contain correspondingly higher concentrations of carbonate.

The most common stratigraphic trend among Metro area lakes is an increase in the inorganic component of the sediments at the expense of organic matter, carbonate, or both around 1860 (according to ^{210}Pb dating) (Fig. 4). As this date corresponds to the rapid expansion of European settlement in the Twin Cities area, the most likely explanation for the change in sediment lithology is a major increase in soil erosion that resulted from the conversion of forest lands to tillage agriculture in the catchments of these lakes. In most cases the decline in organic matter or carbonate content results from dilution by the eroded clastics (silts and clays), and the actual accumulation of organics or carbonates does not decline (see sedimentation rates). This change in LOI is very abrupt in many of the Metro cores (e.g. Dickman, Schultz, Carver), in others it is more subtle (e.g. Turtle, Owasso), and in a few (Christmas, Little Long, Twin -- lakes with high water quality and very small catchments) it is not discernible from other fluctuations that occur before or after 1860. In several of the profiles, the decline in organic matter is reversed further up-core (e.g. Marcott, Little Carnelian), and in many others (e.g. Calhoun, Harriet) there is a notable rise in organic matter just prior to 1860. The median value for inorganic matter increases from 48% in preindustrial sediments to 56% in modern (post-1990) sediments for the Metro group of lakes (Fig. 3)

Cores from the West Central lakes also show marked changes in LOI with the onset of European settlement, but in only half the cases is this seen as an increase in the inorganic fraction (George, Henderson, Long, Kreighle, Sagatagan) (Fig. 4). In the other West Central lakes it is carbonate that increases following settlement (c. 1860), and in most cases the carbonate rise is preceded by an initial pulse of inorganic material (e.g. Dunns, Richardson, Stahls). The increase in sedimentary carbonates likely signals an increase in nutrient inputs and a rise in algal productivity, which could drive calcite precipitation though greater uptake of CO_2 (Engstrom & Swain, 1986; Hodell *et al*., 1998). Those lakes showing a marked rise in sedimentary carbonate have large agriculturally-dominated catchments, while those showing a major increase in inorganic sediments have small catchments with less agricultural land-use. The median value for carbonate content increases from 18% in sediments of preindustrial age to 28% in modern sediments for the group as a whole (Fig. 3).

LOI profiles from the Northeast lakes show little stratigraphic change compared to those from the other two study regions (Fig. 3, 4). Among cores from the North Shore and the Superior National Forest, only Bear, Wolf, and Windy show a perceptible rise in inorganics, and even this change is very small. Large parts of northeastern Minnesota were selectively logged for pine around the turn of the century, and these slight changes in sediment composition may represent subtle shifts in erosion regime occasioned by this transient impact. Four of the five lakes from Voyageurs National Park also show a spike in inorganic matter around 1900, which again is about the time this area was logged. Most cores from the Grand Rapids area (Forsythe, Long, Loon, Snells) show a gradual rise in the inorganic fraction after 1880, which is about the time of European settlement in this part of the state. Little Bass, the fifth lake from this region, is somewhat anomalous in that there is no LOI change until 1935 when carbonate content increases dramatically. The Grand Rapids area lakes are all impacted to some degree by lake-shore homes and agricultural land-use, unlike the other Northeast lakes which have entirely forested catchments.

Lead-210 Dating:

Stratigraphic profiles of total ^{210}Pb range from near exponential (e.g., Locator, Loiten, Shoepack) to highly kinked and non-monotonic (e.g. Fish, Marcott, Carver, Little Carnelian) (Fig. 5). The exponential profiles from many of the Northeast lakes indicate constant sediment accumulation, while the flat sections and reversals evident in most of the Metro and West Central profiles suggest major changes in sediment input over the last 150 years. Supported ^{210}Pb values, indicated by near constant down-core activity, occur at sediment depths ranging from 15 to 120 cm. This depth typically exceeds 50 cm in Metro and West Central lakes and is generally less than 50 cm in Northeast lakes. Supported ^{210}Pb ranges from 0.26 to 3.63 pCi/g among the 50 lakes, although the median is 0.66 pCi/g and most values are less 1.0 pCi/g (Table 4). Lead-210 activity at the sediment surface shows even greater variation than supported ^{210}Pb, ranging from 2.4 to 123.5 pCi/g. These values are highest for the Northeast lakes (median = 33.1 pCi/g), intermediate in the Metro group (median = 18.0 pCi/g) and lowest in the West Central lakes (median = 10.6 pCi/g) (Table 4). Because sediment loading dilutes the ^{210}Pb supply, surface ^{210}Pb activities are inversely related to sediment accumulation rates. Thus the contrast in surface ^{210}Pb among lake groups indicates that present-day sediment inputs to West Central and Metro lakes are much higher than those for the Northeast lakes. The inventories of unsupported ^{210}Pb in the 50 cores range from 15.2 to 70.4 pCi cm^{-2}, with a median value of 27.4 pCi cm^{-2} (Table 4). These values are equivalent to a core-specific ^{210}Pb flux of 0.5 to 2.3 pCi cm^{-2} yr^{-1} (median = 1.0 pCi cm^{-2} yr^{-1}), which is well in excess of the average atmospheric flux of ^{210}Pb for this region (0.45 pCi cm^{-2} yr^{-1}, Urban *et al*., 1990). Such results indicate moderate to substantial sediment focusing, such that core-specific fluxes of Hg (or other sedimentary materials) exceed actual aerial loadings to most of the lakes.

Most of the cores could be reliably dated by the c.r.s. (constant rate of supply) model; only Sweeney (Metro) and Sagatagan (West Central) were exceptions. In the Sweeney Lake profile, ^{210}Pb values at the base of the core (110-140 cm) are higher than those above (Fig. 5), despite the fact that LOI data indicate a clear settlement horizon (c. 1860) at a depth of 100 cm (Fig. 4). Such results indicate that these deeper strata contain only supported ^{210}Pb and that supported activity declines upcore, most likely due to changes in sediment lithology. As ^{226}Ra (and hence supported ^{210}Pb) cannot be measured directly by alpha spectrometry methods, this core remains undateable. The Sagatagan core contains a broad zone of constant ^{210}Pb, Hg_T, and LOI between 18 and 72 cm that likely represents a slump (Fig. 5). As the ^{210}Pb profile above and below this section is approximately exponential, dates were calculated by the cf:cs (constant flux:constant sedimentation) model with the homogenized section removed. The resulting chronology is reasonably consistent with LOI evidence for European settlement around 1860.

Few of the ^{210}Pb profiles show evidence of sediment mixing sufficient to affect the resulting chronologies. Several cores from each region have a surface zone of relatively constant ^{210}Pb (Fig. 5), and while such features could indicate sediment mixing, almost all such sections show stratigraphic detail in either LOI or Hg concentrations that would not be preserved if the sediments had been mixed. In those few cases where the evidence from ^{210}Pb, LOI, and Hg profiles is consistent with mixing (Bean, Bear, August), the portion of the ^{210}Pb inventory that might be homogenized is insufficient (except for Bear) to appreciably alter the chronology obtained by the c.r.s. model. Only for Bear Lake, with its very slow sedimentation rate, was it necessary to include a mixing term in the model.

In most of the cores, dating precision was better than ± 5 years (1 s.d.) for the last century and ± 2-3 years for the most recent 50 years. However, dates for the preindustrial period

have much higher uncertainty, especially for Metro and West Central lakes. For the Northeast lakes, the median error for pre-1860 dates was ± 10 years (IQR = 11 yr), whereas for the Metro and West Central lakes the uncertainty was ± 16 years (IQR = 20 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 (Fig. 6). Among Metro area lakes the rise in sediment flux began sometime after 1860 and was gradual at first. In many cores the increase did not become statistically significant until the late 1800s. Sediment accumulation accelerated dramatically after the turn of the century and reached peak values during the 1940s and 50s in all but two Metro cores (Christmas, Square). Peak sedimentation rates range from 3 to 20 times pre-settlement values. During the last two decades, sediment flux has declined sharply in 14 of the 20 Metro lakes, while remaining high in three others (Johanna, Owasso, Turtle). Only Square Lake does not show a post-settlement increase in sediment flux, which is surprising in light of the large increase in inorganic content of the core after 1860.

The post-settlement increase in sediment accumulation among West Central lakes is similar in timing and magnitude to the Metro group, although four of the ten lakes in this region show a rising flux right up to the present decade (Hook, Dunns, Richardson, Kreighle) (Fig. 6). Four others show a drop from peak values during the last 20-40 years (Diamond, Stahls, Henderson, Long), while the cores from George and Sagatagan reveal no systematic trend in sediment flux over the period of record.

The Northeast lakes also show an increase in sediment accumulation, but one that is later and smaller than in the Metro and West Central groups (Fig. 6). 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. None of the lakes from the North Shore or Superior National Forest (SNF) show a return to pre-logging sedimentation rates, despite the fact that these watersheds reforested quickly and have not been appreciably disturbed since the early 1900s. Wolf Lake on the North Shore and all of the SNF lakes show increasing sedimentation rates during the last 2-3 decades, while sediment flux to the others has leveled off or declined slightly (Dyers). The increase among the Grand Rapids lakes is somewhat higher than elsewhere in northeastern Minnesota, and all of the lakes from this region show a decline in sediment accumulation sometime during the latter half of the 20th century. Lakes from Voyageurs National Park exhibit the smallest change in sediment flux among any in the data set. Locator, Loiten, and Shoepack are essentially constant over time, Tooth records a small increase after 1900, and only Little Trout shows a major rise in sedimentation rates during this century.

Present-day sediment accumulation rates in the 50-lake data set span about two orders of magnitude ranging from 0.05 to 5.0 kg m^{-2} yr^{-1} (Fig. 7, Table 4). With a median value of 0.83 kg m^{-2} yr^{-1} (IQR = 3.21 kg m^{-2} yr^{-1}), the West Central lakes are among the highest, although there is considerable overlap with the Metro group (median = 0.55, IQR = 0.44 kg m^{-2} yr^{-1}), but little with the Northeast lakes (median = 0.22, IQR = 0.13 kg m^{-2} yr^{-1}). These values represent an average increase over preindustrial (pre-1860) sedimentation rates of 540%, 340%, and 100% for the West 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 kg m^{-2} yr^{-1}) and preindustrial (median = 0.05 kg m^{-2} yr^{-1}), and the smallest average increase from

preindustrial to modern (50% compared to 70-160% for the other three subgroups). Sediment accumulation rates for the 20th century have a mean error of 6% (1 s.d.), whereas those representing the preindustrial period (pre-1860) have a much higher uncertainty (mean = 31%). The pre-1860 errors for the Metro and West Central cores are even greater (mean = 49%).

Total Mercury:

Concentrations of Hg_T increase in most cores from a low background in preindustrial sediments (pre-1860) to maximum values sometime during the 20th century (Fig. 8). In many cases the rise is non-monotonic; 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. Calhoun, 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 (Fish, Marcott, Gervais, Carver, Little Carnelian) coincide closely with minima in Hg concentration (Fig. 6, 8). Likewise those West Central cores showing a major rise in post-settlement sediment flux (Diamond, Hook, Stahls, Dunns, Richardson) have steadily declining Hg concentrations during the same period. Although Hg_T concentrations commonly fall during periods of increased sediment flux, the accumulation of Hg almost always rises.

Differences in Hg_T concentrations among lake groups are also closely aligned with rates of sediment accumulation. Sedimentary Hg concentrations are consistently higher in the Northeast group of lakes than in the West Central and Metro lakes, both in preindustrial (pre-1860) and modern (post-1994) times (Fig. 7). The median preindustrial Hg concentration in the Northeast lakes (106 ng/g) is higher than any of the preindustrial values from either the Metro or West Central groups (medians = 41 and 46 ng/g, respectively), and the same is true for modern Hg_T concentrations (medians = 186, 102, and 58 ng/g, for Northeast, Metro, and West Central, respectively). Conversely, sediment accumulation rates are lowest in the Northeast lakes. Within the Northeast group, those lakes from the Grand Rapids area have consistently lower Hg_T concentrations than those from the other three subregions while at the same time having higher sediment accumulation rates. The West Central lakes, which show the smallest increase in Hg_T 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_T 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, an unusually large spike in Hg_T concentration during the 1930s indicates Hg contamination well in excess of that which could be supplied from the atmosphere. Peak concentrations (2100 ng/g) and accumulation rates (2700 $\mu g\ m^{-2}\ yr^{-1}$) for Hg_T 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) and fluxes (480 $\mu g\ m^{-2}\ yr^{-1}$) remain elevated compared to other metro sites. The most likely explanation for these historically enriched sediments is discharge of Hg contaminated wastes (possibly municipal sewage) from the nearby town of Lake Elmo. 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_T show a more consistent pattern among lakes within each region than do concentration profiles (Fig. 8). 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. Dyers, Wilson, Locator, Tooth). In all Metro lakes with the exception of Johanna and possibly Christmas, there is a recent decline in Hg accumulation from peak values during the 1950s to 1970s. In some cases the decline is parallel to a decrease in Hg concentration (e.g. Calhoun, Harriet, Square), 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. Marcott, Gervais, Little Carnelian). 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, although trends in several cores are interrupted by sharp peaks and reversals that appear driven by changing sedimentation rates (e.g. Little Bass, Snells) (Fig. 8). Cores from two of the subgroups (Grand Rapids and Voyageurs) show a consistent decline in Hg accumulation during the last 2-3 decades which coincides (except at Forsythe and Little Trout) with decreasing Hg concentrations. This reversal is not apparent in any of the North Shore or SNF sites with the possible exception of Dyers Lake. Bean and Nipisiquit have more irregular profiles, but recent Hg accumulation rates are near maximum for the period of record at these sites.

In the West Central group, those lakes with highly agriculturalized watersheds (Diamond, Hook, Stahls, Dunns, Richardson), show strong increases in Hg accumulation despite flat or declining Hg concentrations during the period of record (Fig. 8). There is a sharp decline in Hg accumulation around 1940 in the Diamond Lake core and smaller spikes in the other four profiles that derive entirely from changes in sediment flux. Among the other West Central lakes, George, Kreighle, and Sagatagan show a gradual rise in Hg accumulation similar to trends in the Northeast lakes, 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. Median values are 8, 10, and 12 μg m^{-2} yr^{-1} for Metro, Northeast, and West Central groups, respectively, and IQRs are 9, 8, and 10 μg m^{-2} yr^{-1}. This convergence of Hg fluxes indicates that, prior to European settlement and industrialization, Minnesota lakes received similar loadings of Hg_T and that atmospheric deposition was the primary source. Preindustrial rates of atmospheric Hg deposition for the Midwest are estimated at about 3.7 μg m^{-2} yr^{-1} (Swain *et al*., 1992), which is lower than 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 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 West Central lakes (medians = 58 and 56 μg m^{-2} yr^{-1}, respectively) and smallest for the Northeast group (median = 36 μg m^{-2} yr^{-1}). The range of values within each lake group is also much greater (IQRs = 48, 32, 72 μg m^{-2} yr^{-1} for Metro, Northeast, and West Central, respectively), which suggests that factors other than atmospheric Hg deposition are now influencing Hg loading to individual lakes. Ratios of modern to preindustrial Hg accumulation (Hg flux ratios) average 9.8 (s.d. = 10.4) for the Metro lakes, 3.6 (s.d. = 1.4) for Northeast lakes, and 5.6 (s.d. = 2.6) for West Central lakes.

Methyl Mercury:

Concentrations of MeHg in sediments from the Northeast lakes show a similar stratigraphic pattern for 12 of the 15 cores analyzed (excluding Loon, Long, and Elmo).

In these 12 profiles MeHg concentrations are low and relatively stable from preindustrial times to the mid-1900s, rising thereafter to peak concentrations at or near the sediment surface (Fig. 9). The rise in MeHg is irregular in many of the cores and is interrupted by small reversals and flat sections, however, recent concentrations are clearly elevated above background, in some cases by more than an order of magnitude. The mean background concentration for these cores is 0.16 ng/g (s.e. = 0.09 ng/g), while peak concentrations range from 0.3 to 6.2 ng/g.

The recent increase in MeHg exceeds that for Hg_T in these 12 cores, so that MeHg as a percent of Hg_T also rises during the mid 1900s (Fig. 9). In most cases there is a sharp surface peak in %MeHg (e.g. Loiten, Shoepack, Tooth) that likely represents a zone of active Hg methylation/demethylation near the sediment/water interface. However, %MeHg begins to rise at core depths ranging from 7-22 cm, well below the sediment surface, and levels off before climbing sharply in the uppermost 3-4 cm. The timing of the initial rise is relatively similar among lakes ranging from 1939 to 1963, except in Ninemile where it begins in the mid-1970s. MeHg ranges from 0.04% to 0.24% of Hg_T prior to the increase and from 0.2% to 2.1% of Hg_T at peak surface values.

In the cores from Loon and Long, which depart from the above pattern, MeHg concentrations rise immediately after settlement (1880s), drop sharply around 1900, and then increase irregularly thereafter (Fig. 9). In both cores, fluctuations in %MeHg follow closely those for MeHg concentration, indicating that the changes in MeHg concentration are largely independent of those for Hg_T. For example, Hg_T remains relatively constant at the turn of the century when MeHg concentrations decline sharply. Pre-settlement %MeHg values for Loon (0.5%) and Long (1.0%) are similar to their respective present-day (core-top) values, but are substantially higher than background %MeHg for the other 12 cores.

The core from Lake Elmo in the Metro region was also analyzed for MeHg to determine whether the large pulse of anthropogenic Hg in the 1930s was more readily methylated than natural Hg inputs in preindustrial times. The resulting profile shows extremely high concentrations of MeHg (4.6 ng/g maximum) coincident with the 1930s peak in Hg_T but a nearly constant %MeHg (0.2%) throughout the zone of Hg contamination (Fig. 9). %MeHg actually declines follow settlement in the 1860s but remains virtually unchanged from 1900 to 1970. These results suggest that net methylation increased in direct proportion to Hg_T loading and that the sediments faithfully record the historical change in MeHg production. However, it is also possible that MeHg concentrations reflect a post-depositional steady-state between methylation and demethylation and that the spike in MeHg concentration is in effect supported by the spike in Hg_T.

DISCUSSION

Total-Hg and Erosion

Results from this study show historical increases in Hg_T flux at all of the study sites, but the largest increases occur in the Metro and West Central lakes, and the smallest are in the Northeast group (Fig. 7). Likewise, the increase in total sediment accumulation from preindustrial to modern times is highest in the West Central lakes and lowest in the Northeast. The rise in sediment accumulation that follows European settlement at the Metro and West Central sites is typically accompanied by an increase in % inorganic matter, which is composed primarily of detrital silicates from soil erosion (Fig. 4, 6). Because post-settlement land-use changes have been most severe in the Metro and West 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 50-lake data set further illustrates the linkages between erosion rates and Hg flux. Present-day (post-1994) sediment accumulation is strongly correlated with Hg accumulation ($r = 0.84$) but negatively so with Hg concentration ($r = -0.68$) (Fig. 10). These relationships are somewhat weaker in preindustrial strata, especially that between sediment flux and Hg accumulation rates ($r = 0.47$). The negative covariance between sediment flux and Hg concentration is also apparent 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. Dickman, Carver, Dunns; Fig. 8). The sediment source contributing to this change must therefore contain some Hg but less than that of the pre-existing sediment matrix. Undisturbed forest soils in northern Minnesota have an A-horizon Hg content of 100-150 ng/g (Nater & Grigal, 1992) while agricultural soils in the southern part of the state have Hg concentrations of 25-50 ng/g (Balogh, unpublished data). 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 surfaces soils are considerably enriched in Hg_r relative to underlying soil parent material, a build-up attributable to atmospheric Hg deposition (Nater & Grigal, 1992; Grigal *et al*., 1994). The atmosphere is thus the ultimate source for most of the Hg entering Minnesota lakes, either from direct deposition to the lake surface of 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_r flux and total-Al accumulation (a proxy for detrital silicates). Correlation matrices and principal components analysis (PCA with varimax rotation) for the 50-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). This statistical analysis was carried out using GIS data for both total and primary catchments (the primary catchment excludes that portion of the watershed above the outflow from major upstream lakes), but only results for the primary catchment are presented here, as those for the total catchment were very similar.

The first two factors extracted by PCA analysis explain 60- 69% of the variance in the three regional lake data sets. An ordination of factor scores for the Metro region (Fig. 11) shows Hg flux closest to Al-flux and aligned with cover-types for %Built-up and %Road along the first axis and distant from another cluster that includes Slope (mean slope class) and cover types for %Agland (agricultural) and %Forest (sum of deciduous, conifer and mixed forests). The correlations of Hg flux with %Built-up and %Road are both significant ($r = 0.60$ and 0.59, respectively, $p = 0.01$) (Fig. 12, Table 5). These results indicate that urban cover types (built-up and road) contribute more Hg_r to lakes than do rural cover types (agland 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. street runoff, storm sewers) 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 (Fig. 11). Likewise, the negative relationship between Hg flux and %Agland reflects the fact that % cover-type is a closed data set, and catchments cannot simultaneously be built-up and agricultural.

The PCA ordination of the West Central lakes shows almost identical factor scores for Hg and Al fluxes and a close alignment of these two sedimentary variables with %Agland along the first axis (Fig. 11). The other cover types (%Wetland, %Road, %Built-up, % Forest) are distributed widely along axis-2 far distant from this first cluster. The strong correlations between %Agland and Hg and Al fluxes (r = 0.77 and 0.75, respectively) (Table 5) 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 West Central sites; the subgroup of five lakes selected for their agriculturalized catchments (>70% Agland) has modern Hg accumulation rates in excess of 60 μg m^{-2} yr^{-1}, while the other subgroup with more limited agriculture (<40% Agland) has Hg accumulation rates below 50 μg m^{-2} yr^{-1} (Fig. 12). As might be expected, %Agland and steepness of slope are negatively correlated, producing a weakly negative correlation between Hg flux and Slope (r = -0.37) (Table 5). Although Hg flux is only weakly correlated with the other cover types, multiple step-wise regression (backward or forward selection) indicates the %Wetland explains a significant proportion (p = 0.03) of the variation in Hg flux remaining after accounting for differences in %Agland (r^2 = 0.8 for 2-variable model). The coefficient for %Wetland in this 2-variable model is negative, suggesting that wetlands reduce Hg_T loading by trapping particulate-bound Hg.

Hg flux and Al flux are also closely aligned in the PCA ordination of the Northeast data set, but they are well separated along axis-2 from all land-use cover types except %Wetland (Fig. 11), and none of the correlations with land-use are statistically significant (Table 5). Although these fluxes are most closely aligned with the catchment/lake area ratio (C/L), their individual correlations with C/L are very weak (r < 0.2). 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 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 qualities in addition to catchment/lake area ratio may be important determinants of Hg flux to these relatively pristine lakes.

Results from the Metro and West 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 (0.97-1.4 g km^{-2}; 1995-96) were more than twice that of the Mississippi main stem (0.46-0.51 g km^{-2}) or the St. Croix (0.43-0.52g 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 (11-30 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 5.6 for West Central lakes. M/P flux ratios from the Northeast sites range from 2.0-6.7, which is more similar to that reported for other remote North American lakes with undisturbed catchments (Johnson *et al*., 1986; Johnson, 1987; Rada *et al*., 1989; Engstrom *et al*., 1994; Lockhart *et al*., 1995; Lucotte *et al*., 1995). Clearly, Hg inputs to many of the Metro and West 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 game fish (Walleye, Northern Pike) are highest in the northeastern part of the state and low in most West Central and Metro area lakes (Wiener *et al*., 1995), 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 West Central lakes are chemically predisposed to low rates of Hg methylation (high pH, high alkalinity, low DOC) (Swain & Helwig, 1989; Cope *et al*., 1990; Wiener *et al*., 1990; Simonin *et al*., 1994).

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. In order to disentangle increasing watershed inputs of Hg from spatial and temporal trends in atmospheric deposition it is necessary to normalize Hg fluxes for different degrees of watershed impact. Here we use changes in accumulation of total-Al in the sediments as a proxy for erosional intensity to correct the changes in Hg accumulation for Hg inputs from catchment soils. In the first part of this analysis, Hg and Al accumulation rates were computed for each core at two time-stratigraphic periods --- modern and preindustrial. Modern rates were determined from the uppermost core interval and represent the last 1-5 years (mean age = 1994), while preindustrial values represent average accumulation rates prior to 1860). The ratio of Hg accumulation between these two periods (the M/P flux ratio) provides a relative measure of the increase in Hg inputs to the lakes. Flux ratios are independent of individual lake characteristics (size, chemistry, morphometry, etc.) that otherwise affect the absolute flux of mercury to the core-site and can be compared among lakes to assess spatial trends in atmospheric deposition (EPRI, 1996).

There is a reasonable correlation between the M/P flux ratio for Hg and that for Al among lakes in each of the three study regions. Simple linear regression with both variables log-transformed to normalize variance have coefficients of determination (r^2) ranging from 0.76 to 0.87 (Fig 13). These results imply that for a given increase in Al-flux there is a corresponding increase in Hg accumulation and that Hg concentrations of eroded soils are broadly similar among lakes within each region. The critical point in these relationships is that the large range in M/P Hg flux ratios (especially for the Metro and West Central groups) is understandable in light of the large differences among lakes in erosional inputs caused by watershed disturbance; lakes with larger increases in Al flux have correspondingly larger increases in Hg accumulation. Thus increases in Hg accumulation for lakes with M/P Al flux ratios near unity ($\ln [M/P_{Al}] = 0$) represent changes in Hg flux due largely to atmospheric deposition, and the y-intercepts in the regression models are the atmospheric Hg flux ratios predicted from each regional data set.

If we wish to know whether increases in atmospheric Hg deposition have been larger in certain parts of Minnesota, the question to ask is whether the y-intercepts from these regional regression lines are statistically different or not. Regression lines may be compared following methods outlined in Weisberg (1980) by constructing four models in which (1) both slopes and intercepts are different (general model), (2) slopes are equal and intercepts are arbitrary (parallel regression), (3) intercepts are equal but slopes are arbitrary (concurrent regression), and (4) slopes are equal as are the intercepts (coincident regression). A comparison of the residual sum of squares (RSS) of model-2 with that of model-1 tests whether slopes are equal (intercepts arbitrary); a comparison of RSS between model-3 and model-1 tests whether intercepts are equal (slopes arbitrary); and a

comparison of RSS between model-4 and model-2 tests whether intercepts are equal when slopes are the same (analysis of covariance).

Results from this analysis indicate that slopes of the three regression lines in Figure 13 are not significantly different from one another (model-2 vs. model-1; $F_{(2, 41)} = 2.46$, $p = 0.098$), whereas the intercepts are (model-4 vs. model-2; $F_{(2, 43)} = 9.16$, $p = 0.0005$). This difference in intercepts actually lies between the Metro group and the other two regions. A comparison of regression lines between the Northeast and West Central groups shows that both slopes (2, 1; $F_{(1, 26)} = 3.49$, $p = 0.073$) and intercepts (4, 2; $F_{(1,27)} = 1.14$, $p = 0.296$) are not significantly different, while a comparison between Metro and Non-metro (Northeast and West Central combined) indicates very different intercepts (4, 2; $F_{(1,44)} = 18.03$, $p = 0.0001$) but similar slopes (2, 1; $F_{(1, 43)} = 1.03$, $p = 0.316$). A division of Metro lakes according to distance from the urban centers (close vs. distant, Fig. 13) is not significant, nor are differences among individual regression lines for the four Northeast subgroups (Grand Rapids, North Shore, SNF, Voyageurs).

If Al flux ratios properly correct for changes in catchment Hg loading, the conclusion must be that Metro area lakes have experienced larger increases in atmospheric Hg deposition than have lakes in west central or northeastern Minnesota. The y-intercept from model-2 for the Metro group regression line (1.248) is equal to an M/P Hg flux ratio of 3.48 (M/P = exp[y-intercept]), while that for the non-Metro lakes (0.939) represents a flux ratio of 2.56. Although we suggest (above) that erosion may not be the only vector for Hg transport from urban watersheds, the y-intercept is most strongly influenced by lakes with low Al flux ratios, and these same lakes are the least urbanized of the Metro group. A M/P flux ratio of 3.5 is also in line with that reported for other areas of the eastern U.S. (Fitzgerald *et al*., 1998), so it seems unlikely that our calculations substantially under-correct for watershed impacts.

The Hg flux ratio for non-Metro lakes is smaller than that reported by Swain *et al*. (1992) (M/P = 3.4) for seven Minnesota and Wisconsin lakes, four of which were from northeastern Minnesota. The larger increase in Hg flux from their study may partially reflect changes in watershed loads which were not considered in their calculations. However, the lakes that Swain *et al*. studied were largely pristine, and watershed impacts should have been small. Moreover, results from our current study measure Hg deposition rates a decade after Swain *et al*., and thus may reflect additional reductions in Hg loading beyond that reported elsewhere for northeastern Minnesota (Engstrom & Swain, 1997).

A larger post-industrial increase in atmospheric Hg loading to the metro area supports the conclusions of (Glass *et al*., 1998) that present-day Hg deposition in the Twin Cities area is higher than that in outstate Minnesota because of proximity to industrial and residential Hg emission sources. Six years of precipitation sampling (1990-1995) summarized by Glass *et al*. show higher fluxes of Hg in wet deposition near the Twin Cities (8.9 $\mu g\ m^{-2}\ yr^{-1}$ at Bethel) compared to more remote sites in the northeastern part of the state (5.9-6.0 $\mu g\ m^{-2}\ yr^{-1}$ at Ely and International Falls). Such differences are small and may reflect differences in precipitation depth as well as proximity to Hg emission sources in the urban region. Thus confirmation from historical sediment data that Hg deposition rates have risen more in the urban area than outstate provides an essential link between local Hg emissions from the Twin Cities and enhanced Hg deposition to area lakes.

Recent Declines

A related question also addressed in this section is whether recent declines in Hg deposition reported previously for a small subset of Metro and Northeast lakes (Engstrom & 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.

The same approach used above to separate increases in atmospheric Hg deposition from catchment impacts must be applied to recent Hg declines, as many Metro and West Central lakes show changing rates of inorganic sedimentation over the last few decades. In this analysis peak/modern flux ratios (Pk/M) were calculated for the interval of peak Hg accumulation (typically between 1960 and 1980) relative to modern Hg accumulation. Core intervals closest to 1970 were used for those profiles showing no clear Hg peak during the last four decades. Flux ratios for inorganic matter, rather than total-Al, were used as a proxy for erosional change, because Al concentrations were not determined for intervals of peak Hg flux.

Plots of Pk/M flux ratios for Hg against inorganic flux ratios (log-log transformed) show more scatter in the Metro group ($r^2 = 0.55$) than for the West Central lakes ($r^2 = 0.80$) or the Northeast group ($r^2 = 0.86$) (Fig. 14). Nonetheless, a statistical comparison of regression lines shows that both slopes (model-2 vs. model-1; $F_{(2, 41)} = 4.06$, $p = 0.025$) and intercepts (model-3 vs. model-1; $F_{(2, 41)} = 5.94$, $p = 0.005$) are significantly different among the three groups. Again, the difference lies between Metro and Non-metro lakes, as regression lines for the West Central and Northeast groups are effectively coincident (model-4 vs. model-1; $F_{(2, 26)} = 0.29$, $p = 0.75$), while those for the Metro group are distinct from the non-Metro lakes in both slope (2, 1; $F_{(1, 43)} = 8.61$, $p = 0.005$) and intercept (3, 1; $F_{(1, 43)} = 12.13$, $p = 0.001$). The y-intercept for the Metro regression (0.322) is equivalent to a Pk/M Hg flux ratio of 1.38, whereas that for the non-Metro lakes (0.03) is equal to a Pk/M ratio of 1.03.

This analysis indicates that there has been a roughly 30% decline in atmospheric Hg flux to lakes in the Twin Cities area since peak deposition rates of the 1960s and 70s. 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 & Swain, 1997). 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. The conclusion (above) that current rates of atmospheric Hg deposition exceed those in outstate regions indicates that further improvements from local emission reductions are still possible.

The Pk/M flux ratio for non-Metro lakes (1.03) would suggest that Hg deposition rates have not declined in recent years, contrary to conclusions reached earlier by Engstrom and Swain (1997). However, if the Northeast group is divided by subregion, it is apparent that lakes in the Grand Rapids area and Voyageurs National Park have consistently higher Pk/M Hg flux ratios than lakes from the North Shore or Superior National Forest (Fig. 14). A regression analysis of $Pk/M_{[Hg]}$ vs. $Pk/M_{[Inorganic]}$ indicates that both slopes (2, 1; $F_{(2, 14)} = 5.71$, $p = 0.015$) and intercepts (3, 1; $F_{(2, 14)} = 39.8$, $p < 0.0001$) are different among the four subgroups. The y-intercepts for the North Shore and SNF lakes are equivalent to a Pk/M flux ratio of 1, which indicates no recent decline in Hg flux for these lakes. The Grand Rapids subgroup, on the other hand, has $Pk/M_{[Hg]}$ flux ratio of 1.28, while the Voyageurs lakes have a flux ratio of 1.18.

These results indicate that Hg deposition has declined in the Grand Rapids and Voyageurs Park areas by 15-20% since the mid-1970s, but not at all in other parts of

northeastern Minnesota or in the west central part of the state. The localized nature of the decline implies a reduction in nearby Hg emissions sources as opposed to the regional/continental reductions that we envisioned in our earlier study (Engstrom & Swain, 1997). Although U.S. industrial Hg consumption has declined markedly in the last few years, Minnesota is at the low end of a Hg contamination gradient across the Great Lakes states (Nater & Grigal, 1992), and the impact of nation-wide Hg reductions may be discernible only closer to emission sources. On the other hand, there is some evidence from the North Shore and West Central lakes that state-wide Hg deposition may have leveled off in recent years. Many of the Hg profiles from these regions flatten out or fluctuate irregularly during the last 2-3 decades, rather than increase monotonically (Fig. 8). The response of Hg accumulation in lake sediments might also 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 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.

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 as $Hg(0)$. 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 342 t/year in 1954 and declined to near zero by 1980 (Engstrom & Swain, 1997). At peak use, potential Hg emissions from fungicides exceeded that for coal combustion by an order of magnitude. The pulp/paper industry represents the one local Hg source that is common to both Grand Rapids and Voyageurs Park, but absent from the North Shore and SNF subregions. Further evidence that historical use of mercuric fungicides may be responsible for local declines in Hg deposition comes from an ombrotrophic peatland near the Potlatch paper mills at Cloquet (Benoit *et al*., 1994). Here average Hg accumulation rates in five peat cores decreased from 37.8 to 24.5 $\mu g\ m^{-2}\ yr^{-1}$ between 1950-1980 and 1980-1991.

Minnesota Power's Clay-Boswell plant at Cohasset, 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. com.) show coal consumption rising stepwise from 0.4 MT in 1965 to about 3.5 MT in 1981 and leveling off thereafter (Fig. 15). The step increases in 1973 and 1980 represent start-up of units 3 and 4, 350 and 525 MW boilers equipped with tall stacks. Based solely on coal consumption (assuming 0.1 mg Hg/kg coal), potential Hg emissions have remained relatively flat since 1981 (ca. 350 kg/yr). However, controls on SO_2 and particulate emissions during the last two decades may have reduced actual Hg emissions, while increased stack height may have encouraged long-distance Hg transport while reducing local deposition.

Enhanced Hg Methylation

Fifteen cores (all but one from northeastern Minnesota) were analyzed for MeHg to determine whether MeHg accumulation has kept apace with the flux of Hg_T or whether it has increased even more so because of historical increases in net methylation rates.

Almost all of the analyzed cores show a systematic increase in the methylated portion of Hg_T (%MeHg) sometime between 1940 and 1970, a change that is unprecedented back to preindustrial times (Fig. 9). %MeHg rises even more sharply in a number of cores just below the sediment-water interface.

The first challenge is to determine whether these increases represent historic changes in methylation rates or whether they are simply diagenetic features that move upwards as new sediment accumulates. The surface peaks are particularly suspicious, both by their abruptness and size and because they are difficult to explain in historical terms. Other studies of intact sediment cores from lakes and wetlands show a consistent pattern of surface MeHg maxima that are coincident with peak rates of microbial methylation and demethylation at the sediment-water interface (Gilmour *et al*., 1992; Ramlal *et al*., 1993; Gilmour *et al*., 1998; Marvin-Dipasquale & Oremland, 1998). MeHg concentrations in surface sediments vary seasonally as well, with maximum levels typically building toward late summer, either from net *in situ* methylation or possibly the accumulation of MeHg from seston deposition (Regnell *et al*., 1997). Such results strongly imply that surface MeHg peaks are transient features that reflect a dynamic balance between MeHg formation and degradation. It is less likely that surface peaks are generated by upward diffusion within the sediment profile, given the strong affinity of MeHg for the particulate phase (log K_d between sediments and pore waters = 10^4 - 10^5; Hurley, unpublished). Additionally, long term (27 month) sediment mixing - incubation experiments (Hurley, unpublished) showed little diffusive redistribution of MeHg below the upper 2 cm, although surface peaks reappeared in homogenized cores with the accumulation of new MeHg. Thus surface enrichment of MeHg, either from *in situ* methylation or seston deposition, and subsequent demethylation or diffusion to the overlying water (Regnell *et al*., 1997; Gilmour *et al*., 1998) provide the best explanation for surface MeHg peaks.

A stronger case can be made that the mid-1900 increase in %MeHg represents a historical change in net methylation. This initial rise occurs well below the surface of most cores (7-22 cm) and reaches a plateau that is broadly synchronous among lakes with very different rates of sediment accumulation (Fig. 9). Such temporal concordance argues more strongly for a historical change in MeHg production than do the surface peaks, and the depth at which the change occurs is more difficult to explain by post-depositional processes. Substantial diffusion seems unlikely in light of both Hurley's results (above) and the sharp stratigraphic detail in MeHg concentration at depth in many of the cores from this study. The abrupt declines in MeHg in Long and Loon lakes (c. 1900), for example, would have been obliterated by rapid diffusion of MeHg. The large spike in MeHg in the Lake Elmo profile (c. 1930) is likewise instructive, because it is highly unlikely that %MeHg would have remained constant across this Hg contaminated interval if diffusion (upwards or downwards) had occurred. Alternatively, it is possible that the mid-1900 increase in %MeHg results from a slow net degradation of MeHg following sediment burial. However, such a mechanism is hard to reconcile with the stable MeHg baseline evident in most cores. Near constant values for MeHg (prior to 1940) suggest that methylation/demethylation rates eventually reach steady state. It also seems unlikely that progressive demethylation would result in a temporally concordant increase in %MeHg across such a wide array of sediment cores.

The final piece of evidence that MeHg profiles record historic changes in MeHg production comes from three lakes (Loon, Long, Elmo) that show sharp up-core declines (rather than increases) in %MeHg (Fig. 9). These declines occur at about the time of European settlement (c. 1880 at Long and Loon; 1860 at Elmo) and are coincident with a rise in sediment flux caused by local land-use changes. The other lakes with MeHg profiles have largely undisturbed catchments. The change in %MeHg is opposite that

which might be expected if MeHg were progressively degraded over time, and the synchronicity with local events argues for a historic, rather than diagenetic, cause. Methylation rates may have declined because of more rapid sediment burial, changes in sedimentary redox conditions, or inputs of less reactive (e.g. soil-bound) Hg. Regardless of the mechanism, these results imply that MeHg profiles are relatively stable, at least below the surface zone of active methylation/demethylation.

Assuming that the mid-1900 rise in %MeHg is historical, the change in net methylation represented by the increase can be estimated as the ratio of recent to baseline (R/B) %MeHg. Baseline %MeHg is the mean background value from preindustrial times up to the start of the mid-1900 rise. The date of increase has some uncertainty depending on sample frequency over the period of change (Fig. 16), and is arbitrarily set at 1954 (the average of the other lakes) for Long and Loon, where a rise in %MeHg is difficult to discern against high background variability. Recent %MeHg is the average of values including the first discernable rise above baseline, but excluding surface peaks in the upper 1-7 cm. Lake Elmo is excluded from these calculations because of the likelihood of historical Hg contamination from local point-sources. Baseline %MeHg ranges from 0.04 to 0.24% for all sites except Long (1.05%) and Loon (0.53%), while recent %MeHg ranges from 0.09 to 0.95% (Fig. 16). The ratio of these two values (recent/baseline) varies from 1 to 4 with most lakes showing a relative increase of 2-3.

Although there is substantial uncertainty in some of these ratios (from %MeHg variability and ambiguous cutoff dates), taken as a whole they imply at least a doubling of net MeHg production in most of the lakes during the last 3-5 decades. This increase coupled with the 3-fold rise in Hg_T flux means that potential biological exposure to MeHg toxicity in these lakes today is more than six (and in some case more than ten) times what it was preindustrially. An increase in MeHg exposure of this magnitude, especially one that is focused on the last half of this century, is more consistent with the large post-1940s rise in fish-Hg reported for some Minnesota lakes (Swain & Helwig, 1989) than is a more gradual 3x increase implied by sedimentary records for Hg_T. This interpretation also means that current MeHg contamination of Minnesota lakes is far greater than previously thought, and that few if any of the state's lakes would carry fish (Hg) consumption advisories under conditions of preindustrial MeHg exposure.

If our interpretations are correct, and Hg methylation has increased historically in some lakes, what are the likely causes? As the lakes in question are relatively pristine and remote from direct human impact, the logical place to look is towards other atmospheric contaminants that might enhance net methylation rates either within the lakes or their catchments. Experimental studies by Gilmore *et al*. (1992; 1998) provide strong evidence that microbial Hg methylation is sulfate limited in some lakes and wetlands, especially dilute, low ANC waters such as those in our northeastern study lakes. Gilmore *et al*. (1992) point out that sulfate reducing bacteria are important mediators of Hg methylation in lacustrine systems and suggest that historic increases in atmospheric sulfate loading could account for increased MeHg bioaccumulation in sulfate-limited lakes. It has also been suggested that microbial Hg methylation is enhanced by the availability of organic carbon, especially in newly created reservoirs (Heyes *et al*., 1998). If so, atmospheric nitrate deposition, now recognized as a serious global problem (Vitousek *et al*., 1997), might increase the flux of labile carbon through oligotrophic (N-limited) systems and thereby indirectly increase Hg methylation. Many northeastern Minnesota lakes are probably N-limited (Axler *et al*., 1993). However, experimental studies indicate that nutrient additions (nitrate or phosphate) at near-ambient levels have little direct effect on microbial methylation in wetland sediments (Gilmour *et al*., 1998; Marvin-Dipasquale & Oremland, 1998).

Such results imply that the magnitude of enhanced methylation should vary among lakes depending on factors that limit microbial activity, especially that of sulfate reducers (e.g. temperature, sulfate, organic carbon). This expectation is partially borne out by a comparison of R/B %MeHg with water chemistry variables for the northeastern lakes. Although the increase in %MeHg is only weakly related to sulfate ($r = 0.35$), correlations with alkalinity (ln ANC; $r = -0.78$), pH ($r = -0.73$), DOC ($r = 0.63$) and color ($r = 0.71$) are all strong. In a stepwise regression model (forwards or backwards selection), 85% of the variance in R/B %MeHg is explained by three independent variables, ln (ANC), color, and chlorophyll-a (all highly significant, $p \leq 0.01$); coefficients for ANC and chl-a are negative while that for color is positive. These are effectively the same water-chemistry variables that are frequently correlated with MeHg levels in fish (Swain & Helwig, 1989; Cope *et al*., 1990; Wiener *et al*., 1990; Simonin *et al*., 1994).

As there is little evidence for atmospheric acidification of Minnesota lakes (Twaroski *et al*., 1989), it is unlikely that Hg methylation has been enhanced directly by changes in either ANC or color (DOC). Instead, these variables depict a predisposition toward enhanced methylation from some other forcing. Although lake sulfate levels are not a good predictor of enhanced methylation, the strongly negative correlations with ANC and pH indicate that the more dilute lakes have experienced the largest change in Hg methylation. Low ANC lakes are typically low in sulfate, and ANC may be a better predictor of sulfate limitation at the sediment surface than are sulfate concentrations in the epilimnion. Hence, sulfate stimulation may still be responsible for enhanced methylation in these systems. Highly colored (high DOC) lakes also show greater increases in %MeHg than do clear-water lakes, which may signify enhanced Hg methylation by wetlands within the catchment. Wetlands are a major sources for both DOC and MeHg to boreal lakes (Driscoll *et al*., 1995; St. Louis *et al*., 1996; Driscoll *et al*., 1998), but those in northeastern Minnesota are typically low in sulfate and hence may be susceptible to enhanced methylation from increased inputs of atmospheric sulfate. Finally, the negative effect of chlorophyll-a (after accounting for ANC and color) indicates that the more oligotrophic lakes have experienced larger increases in %MeHg. If methylation rates are carbon limited anywhere, it should be in these low-productivity waters where the effects of atmospheric nutrient (nitrate) loading on carbon fixation would be strongest. Whether these lakes have actually been impacted by recent nutrient inputs is currently being evaluated through diatom-trophic reconstructions from the same sediment cores used in this study.

Historical increases in both sulfate and nitrate deposition are broadly contemporaneous with the 1940-1970 increase in %MeHg in these sediment cores. Differences in timing among lakes may actually reflect different sensitivities of microbial communities to external forcing from atmospheric deposition. Although such correlations point to plausible mechanisms for enhanced methylation, the link to atmospheric deposition is still tenuous. There may be other explanations – e.g. climate change, beaver impoundments (Johnston & Naiman, 1990; Driscoll *et al*., 1998) – or quite possibly, as argued above, the MeHg increases may not actually be historical. Additional studies are clearly needed to evaluate the stability of MeHg in buried sediments and the depth at which net MeHg production is actually "locked" into the sediment record. Experimental determinations of Hg methylation and demethylation rates under ambient conditions along with laboratory and field-scale manipulations of sulfate and nutrient inputs are also needed to resolve key questions about anthropogenic enhancement of Hg methylation in lakes and wetlands.

SUMMARY

Total-Hg and Erosion

1. An evaluation of historical Hg accumulation in the sediments of 50 Minnesota lakes indicates that Hg_T 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 $\mu g\ m^{-2}\ yr^{-1}$ (median = 9 $\mu g\ m^{-2}\ yr^{-1}$) and showed little regional differentiation. Hg accumulation rates rose steadily in all cores following European settlement and regional industrial development, although concentrations of Hg were depressed in many Metro and West Central lakes by dilution from eroded soils.

2. Hg accumulation rates (both past and present) in all three regions are strongly correlated with the flux of total-Al, a tracer for soil erosion. Present-day accumulation rates for Hg_T are significantly higher in the Metro and West Central regions (medians = 58 and 56, respectively) than in the Northeast (median = 36 $\mu g\ m^{-2}\ yr^{-1}$), largely because of erosional inputs of soil-bound Hg from disturbed catchments. The additional load of Hg is primarily of atmospheric origin.

3. A comparison of GIS-based watershed parameters with modern Hg-accumulation displays a strong relationship between the percentage of built-up cover-types in Metro-lake catchments and the flux of Hg_T to the sediments. In the West Central region, the percentage of agricultural land-use is the strongest determinant of sediment Hg accumulation, followed by wetland coverage, which tends to reduce Hg flux to these lakes.

4. Watersheds in the Northeast region are largely forested, and none of the correlations of Hg accumulation with land-use is significant. The ratio of catchment to lake-surface area (C/L) in the Northeast is only weakly related to Hg accumulation, contrary to previous findings for this region (Swain *et al*., 1992), largely because Hg flux data from this study are based on single (rather than multiple) cores and do not correct for sediment focusing.

5. The increases in Hg accumulation from preindustrial to modern times (M/P flux ratios) are substantially higher in the Metro and West Central regions (mean = 9.7 and 5.6, respectively) than in the Northeast, where M/P flux ratios (mean = 3.6) are more similar to those reported for other remote North American lakes. Hg levels in game fish are highest in the Northeast lakes, indicating that the additional load of soil-bound Hg to Metro and West Central lakes may not result in greater bioaccumulation of MeHg.

Trends in Atmospheric Hg Deposition

6. To determine whether atmospheric Hg deposition varies across Minnesota, Hg flux ratios were normalized to flux ratios for total-Al to correct for changes in Hg inputs caused by soil erosion. Results indicate that Metro area lakes have experienced larger post-industrial increases in atmospheric Hg deposition than have lakes in west central or northeastern Minnesota.

7. Atmospheric Hg deposition in the Metro region is currently about 3.5 times what it was in preindustrial times, while present-day Hg deposition in west central and northeastern Minnesota is about 2.6 times greater than preindustrial. These results indicate that present-day Hg deposition in the Twin Cities area is higher than that in rural Minnesota because of Hg emissions from local urban sources. The Hg flux ratio for non-Metro lakes is somewhat smaller than that reported previously for northeastern

Minnesota. This difference may reflect recent declines in Hg deposition or the fact that previous estimates were not corrected for erosional changes.

8. This analysis also confirms previous observations that atmospheric Hg deposition in the Twin Cities and certain parts of outstate Minnesota has declined during the last few decades. In the Metro area, the decrease has been about 30% of peak deposition rates in the 1960s and 1970s, indicating substantial reductions in local Hg emissions from light industry, residential heating, waste incineration, and other diffuse sources. This decline coupled with reduced erosional inputs has cut Hg loading to many Metro lakes by more than half.

9. Recent declines in Hg deposition to non-Metro study sites appear restricted to lakes in Voyageurs National Park and the Grand Rapids area. The decrease, representing 15-20% of peak Hg loading, is not evident in west central Minnesota or elsewhere in the Northeast (North Shore or Superior National Forest sites). The localized nature of the decline implies a reduction in nearby Hg emissions, rather than the regional/continental-scale reductions suggested by earlier studies. The historical use of mercuric fungicides by local paper mills is the most likely explanation for recent declines in Hg loading to lakes in Voyageurs National Park and the Grand Rapids area.

Enhanced Hg Methylation

10. In 12 of 14 cores analyzed from northeastern Minnesota, the methylated portion of Hg_T (%MeHg) increases above a stable baseline between 1940 and 1970. This increase is thought to represent a historical change in MeHg production that is independent of the flux of Hg_T. Most cores also exhibit a sharp surface peak in %MeHg that is likely diagenetic.

11. The ratio of recent (excluding surface peaks) to background %MeHg ranges from 2 to 3 in most lakes, implying at least a doubling of net methylation during the last 3-5 decades. This increase coupled with the 3-fold rise in Hg_T flux represents a potential biological exposure to MeHg that is more than 6x preindustrial levels.

12. The relative increase in %MeHg in the 14 lakes is strongly correlated with water-chemistry variables that are commonly associated with elevated MeHg levels in fish (low pH and ANC, high DOC and apparent color). A regression model that includes ANC, color, and chlorophyll-a explains 85% of the variance in the relative increase in %MeHg. These variables depict a predisposition to enhanced methylation and point to possible mechanisms for historical changes in net MeHg production.

13. Increased deposition of other atmospheric contaminants, particularly sulfate and nitrate, is the most likely cause for enhanced methylation in these remote, relatively pristine lakes. Historic increases in atmospheric sulfate loading may have increased Hg methylation by sulfate reducing bacteria in sulfate-limited (low ANC) lakes or their surrounding wetlands. Likewise, nitrate deposition may have increased the flux of labile carbon to the sediments of N-limited lakes, thereby increasing microbial activity and net Hg methylation.

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FIGURES

Figure 1. Location of study lakes in Minnesota; key to lake names in Table 2.

Figure 2. Box plots of GIS parameters and water chemistry data for 50 study lakes by region. Rectangles are bounded by the 25th and 75th percentiles; whiskers depict 10th and 90th percentiles.

Figure 3. Box plots of organic, carbonate, and inorganic content of modern (post-1990) and preindustrial (pre-1860) sediments by study region.

Figure 4. Loss-on-ignition profiles for sediment cores. ^{210}Pb dates corresponding to the onset of European settlement in each region are indicated by dashed lines; (a) Metro, (b) Northeast, (c) West Central.

Figure 5. Total ^{210}Pb activity plots for sediment cores. Supported ^{210}Pb indicated by dashed line; error bars represent ± 1 s.d; (a) Metro, (b) Northeast, (c) West Central.

Figure 6. Sediment accumulation rates vs. sediment age as determined by ^{210}Pb dating; (a) Metro, (b) Northeast, (c) West Central.

Figure 7. Box plots of sediment accumulation rates and total-mercury (Hg_T) concentrations and accumulation rates for 50 study lakes by region.

Figure 8. Dated sediment profiles of Hg_T concentrations and accumulation rates for 50 study lakes; (a) Metro, (b) Northeast, (c) West Central.

Figure 9. Dated sediment profiles of methylmercury (MeHg) concentrations and MeHg as a percentage of total Hg (%MeHg) for 14 Northeast lakes and Lake Elmo in the Metro region.

Figure 10. Relationships between sediment accumulation and Hg_T concentration and accumulation among 50 study lakes for modern (post-1990) and preindustrial (pre-1860) periods.

Figure 11. Principal components ordination (varimax rotation) of GIS watershed parameters and the flux of Hg_T and total-Al in sediments of the study lakes.

Figure 12. Relationship between land-use cover types and present-day Hg accumulation in sediment cores from the Metro and West Central lakes. Primary (1°) watershed and cover types defined in text.

Figure 13. Regression of modern/preindustrial (M/P) Hg flux ratios vs. M/P flux ratios for total-Al (a tracer for soil erosion). "Close" lakes are located within 10 km of the centers of Minneapolis or St. Paul ; "Distant" lakes located in rural landscapes further from the urban core.

Figure 14. Regression of peak/modern (Pk/M) Hg flux ratios vs. Pk/M flux ratios for inorganic matter (a tracer for soil erosion). Peak Hg fluxes correspond to the 1960s and 1970s.

Figure 15. Historical trends in SO_2 emissions, coal combustion, and potential Hg emissions from Minnesota Power's Clay-Boswell power plant in Cohasset, Minnesota. Potential Hg emissions assume an Hg content of 0.1 mg/kg coal.

Figure 16. Date and depth at which %MeHg rises above a stable baseline in 14 cores from northeastern Minnesota. Average values for recent and baseline %MeHg and their ratio for the 14 cores; error bars represent ± 1 s.d. Recent values exclude diagenetic peaks present at top of some cores. The date of increase is arbitrarily set at 1954 (the average of the other lakes) for Long and Loon (see text).

Figure 17. Relationship between water-chemistry variables and the increase in mean %MeHg from background values in sediment cores from 14 Northeast lakes.