

## Anthropogenic Copper Inventories and Mercury Profiles from Lake Superior: Evidence for Mining Impacts

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**ABSTRACT.** During the past 150 years, the mining industry discharged more than a billion tons of tailings along Lake Superior shorelines and constructed numerous smelters in the watershed. Given the vast size of Lake Superior, were sediment profiles at locations far offshore impacted by nearshore activities? Did copper and associated precious metal mining modify regional fluxes for copper and mercury? Samples from thirty sediment cores document that background concentrations of copper are high (mean  $60.9 \pm 7.0 \mu\text{g/g}$ ), due to the proximity of natural ore sources. Anthropogenic inventories uncorrected for focusing also are high, ranging from 20 to  $780 \mu\text{g/cm}^2$  (mean  $187 \pm 54 \mu\text{g/cm}^2$ ). Focusing factor corrections decrease the mean estimate and reduce variance ( $144 \pm 24 \mu\text{g/cm}^2$ ). Several approaches to estimating inputs suggest that only 6 to 10% of historic copper deposition originated directly from atmospheric sources, emphasizing terrestrial sources. Moreover, coastal sediment cores often show synchronous early increases in copper and mercury with buried maxima. Around the Keweenaw Peninsula, twenty-two cores trace high copper and mercury inventories back to mill and smelting sources. Direct assays of ores from thirteen mine sites confirm a natural amalgam source of mercury in the stamp mill discharges. Core records from inland lakes (Michigamme Project) also reveal patterns of copper and mercury inputs from a variety of mining sources: historic tailing inputs, amalgam assay releases, and atmospheric smelter plumes.

**INDEX WORDS:** Lake Superior, copper, mining, mercury, sediment.

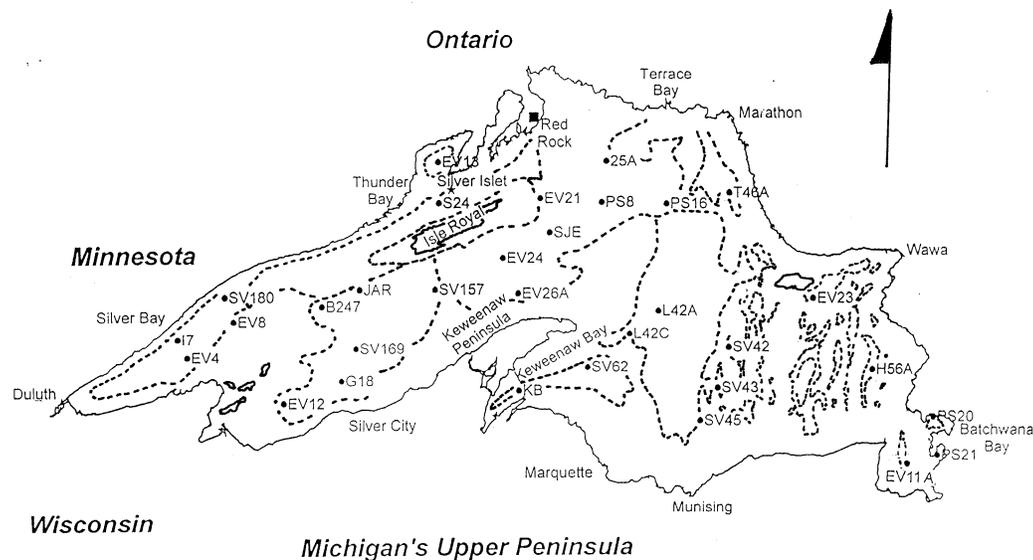
### INTRODUCTION

The Great Lakes ecosystem is susceptible to loading of trace metal contaminants from both terrestrial and atmospheric sources, yet the relative importance of various sources and the details of cycling in nearshore and offshore environments are poorly understood (Galloway *et al.* 1982, Hong *et al.* 1996). Patchy industrial discharges react with shoreline, wetland, and forest ecosystem components. For example, in the dilute waters of Lake Su-

perior, contaminants from shoreline or atmospheric sources move between solid and dissolved phases, adsorb onto settling organic particulate matter, and become buried in sediments. One beneficial consequence of this process is that sediment cores offer excellent opportunities for reconstructing contaminant loading histories (Edgington and Robbins 1976, Christensen and Osuna 1989). However, the sediment inventories of large lakes are often spatially heterogeneous, reflecting site-specific inputs and the long-term consequences of sediment movement. How to utilize sediment cores to clarify inputs and to provide insight into element cycling is a

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## Lake Superior Station Locations



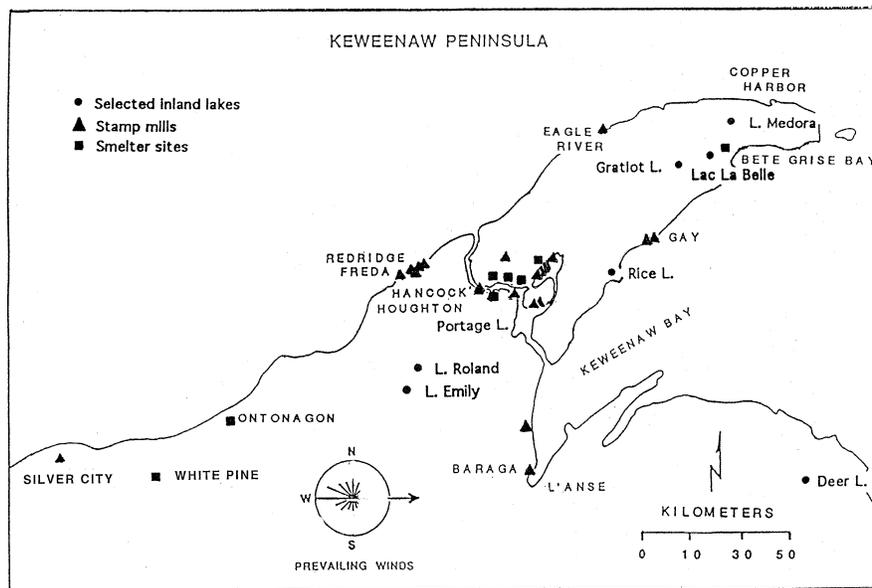
**FIG. 1.** Lake Superior drainage basin showing the location of 30 1983 NOAA inventory cores plus the location of an additional core (EV11A).

challenge (Galloway and Likens 1979, Galloway *et al.* 1982).

The IJC (1989) asserts that 95% of the contaminants which enter Lake Superior come from long-distance atmospheric deposition. While many organic compounds are subject to long-distance transport, copper and mercury loadings may be much more closely associated with regional watershed activities than previously suspected. Early calculations apparently incorporated some serious errors, and previous coring efforts failed to detect important coastal patterns. Two early investigators of Lake Superior sediments, Nussman (1965) and Kemp *et al.* (1978), suspected that copper enrichments in Lake Superior sediments came from several intensively mined regions: The Keweenaw Peninsula of Michigan; Thunder Bay, Marathon, and Sault Ste. Marie regions of Ontario, Canada (Fig. 1). Values near the Keweenaw Peninsula coincided with the path of the Keweenaw Current, suggesting that copper-rich sediments were transported considerable distances from their original sources by currents or ice rafting (Kerfoot *et al.* 1994).

Investigations initially concentrated on the Keweenaw Peninsula region (Fig. 2), where a half billion metric tons of copper mine tailings were discharged into rivers, the interconnected Ke-

weenaw Waterway system, and into Lake Superior between 1850 and 1968 (Kerfoot *et al.* 1994). Kerfoot *et al.* (1994) presented an extensive geographic discussion of these historical discharges. Beaches near many Keweenaw Peninsula towns consist of tailing fans that erode by wave action and that redeposit coarse and fine-grained material along the shoreline and into deeper waters. These tailings are stamp sands, i.e., crushed basalt and conglomerate, that are distinctive in color, mineral content, and physical characteristics from natural lake sediments. Deposits of stamp sand material near mill sites and along the Keweenaw Waterway contain copper in concentrations that locally average 850 to 3,750  $\mu\text{g/g}$  (Kraft and Sypniewski 1981, Kerfoot and Robbins 1999). In addition, 50 million metric tons of mine tailings were discharged directly into Lake Superior along the western coastline (Freda/Redridge region) of the Keweenaw Peninsula by five stamp mills that operated between 1895 and 1968 (Champion, Trimountain, Adventure, Baltic, and Atlantic Mills; Babcock and Spiroff 1970, Kerfoot *et al.* 1994). Smaller amounts were released from Eagle River and Copper Harbor. Along the eastern coastline of the Keweenaw Peninsula, 23 million metric tons were sluiced into Keweenaw Bay at Gay between 1902 and 1932, with other



**FIG. 2.** The Keweenaw Peninsula region illustrating a) the position of stamp mills, smelters, and Michigan Project lakes (round symbols). Prevailing wind direction (west) is indicated in lower left.

smaller inputs occurring at Bete Grise Bay and L'Anse Bay (Mass, Michigan Mills).

To what extent did mining activities in the Lake Superior watershed disturb the entire lake ecosystem and continue to this day to influence metal cycling? How important and widespread are mining signatures in sediments, and what is the relationship with long-distance and localized atmospheric inputs? Thirty inventory cores taken from Lake Superior by NOAA in 1983 (Fig. 1) were analyzed for copper and mercury. These cores provided a much more extensive coverage of Lake Superior than previous efforts (six sampling sites of Kemp *et al.* (1978) or of Kolak *et al.* (1998)). The cores allowed calculation of copper inventories and examination of associations between copper and mercury profiles from a wide variety of depositional environments. Sites were distributed throughout the lake basin and included nearshore bays and eastern trough sediments, suspected sites of high sedimentation. Cesium-137 inventories were used to correct for sediment focusing effects, a technique not available to Kemp *et al.* (1978). A second set of twenty-two additional cores from nearshore environments (Keweenaw Waterway, L'Anse Bay) permitted tracing high copper and mercury inventories back to shoreline sources. An independent, third set of cores from small, isolated inland lakes

(Michigan Project) allowed inspection of localized sediment profiles that result from different types of mining-related activities (stamp mill tailings, smelter plumes, assay laboratory discharges).

## METHODS AND MATERIALS

### Offshore Inventory Cores and Focusing Factor Corrections

Offshore sediment core samples were provided by the NOAA Great Lakes Environmental Research Laboratory from cores originally collected at 30 stations in 1983. The cores were taken from the R/V *Limnos* as part of a National Water Research Institute program (study leader Rick Bourbonniere) and archived. The core sampling sites were distributed over several sedimentation basins (Fig. 1): Duluth Basin (I7, EV4, EV8, SV180), Thunder Bay Basin (S24, EV13), Chefswet Basin (EV12, G18, SV157, SV169, B247, JAR), Isle Royale Basin (EV21, EV24, EV26A, SJE, PS8, 25A, PS16), Marathon Basin (T46A), Keweenaw Basin Trough (KB, SV62), Caribou Basin (L42C, L42A), Lake Superior Troughs (SV42, SV43, SV45), Wawa Trough (EV23), Batchwana Bay (PS20), Goulais Bay (PS21), and Whitefish Bay (EV11A). Cores were obtained with a 7.6 cm diameter gravity corer which did not free-fall, but was carefully lowered

into the sediment, minimizing loss of surface layers and reducing compaction artifacts. All cores were sectioned immediately upon retrieval. The majority of the cores were sectioned at 2 cm intervals to a depth of 20 cm. Selected cores were sectioned at 0.5 cm intervals to a depth of 10 cm and at 1 cm intervals thereafter.

Sediment subsamples for metals analysis were air dried and then homogenized by grinding to a fine powder with a mortar and pestle. A small aliquot (< 0.25 g) of each sample was placed into a pre-weighed Teflon digestion vessel. Ultrapure nitric acid solution (25 mL of 10% v/v) was added to each vessel and the vessels tightly capped and re-weighed. The samples were digested using a CEM microwave digester at 100% power for 10 minutes followed by 50 minutes at 75% power. The vessels were reweighed to insure that no loss of liquid occurred during the digestion process. The contents of the vessels were then filtered using 47 mm Gelman Supor-450 filters and the filtrate transferred to 60 mL acid-leached storage bottles.

The samples were analyzed for copper, silver, and zinc by flame atomic absorption spectrophotometry using a Perkin-Elmer model 5000 atomic absorption spectrophotometer. The samples were analyzed for total mercury by the cold vapor technique using a Perkin-Elmer atomic absorption spectrophotometer and a Perkin-Elmer MHS-20 mercury/hydride system. With this method the mercury is reduced to the elemental form using stannous chloride and then collected as an amalgam on gold foil which is heated rapidly, removing the mercury as a concentrated spike.

#### Keweenaw Inventory Cores

Twenty-two 5.1 cm diameter sediment cores were obtained from the Keweenaw Waterway and nearshore regions of the Keweenaw Peninsula during 1996 and 1997, using a Phleger-type KB gravity corer (Fig. 2). Water sampling depths ranged between 12 and 20 m. The core sites extend from Keweenaw Bay into the interior reaches of the Keweenaw Waterway. The coring device was lowered from one of two boats, the 9.5 m RV *Navicula* and a 5.2 m Boston Whaler. A Lowrance model X-16 sonar unit with tape printout helped position the corer 3 to 4 m above sediments prior to release. Cores were plugged, capped, and transported to Portage View Hospital where they were x-rayed for slime varve stratigraphy, which provides detailed time-stratigraphic information (Kerfoot *et al.* 1994).

Cores were sliced into 2 cm sections and analyzed for Cu, Ag, and Hg. Element analysis followed methods outlined above. In addition, copper ore samples from fourteen mine sites (poor rock pile samples and archived museum ore samples) were assayed for mercury concentrations.

#### Quality Assurance

Standard reference materials (SRM) and replicated samples provided QA/QC information for copper and zinc analyses. Standard Reference Material for the LS 83 samples (copper and zinc analysis) was SRM 2704 (Buffalo River sediment from the National Bureau of Standards). Copper recovery (N = 20) was  $93.18 \pm 7.07\%$ , Zn  $92.03 \pm 5.28\%$ . Replicate Cu samples (N = 20) from cores were  $90.42 \pm 4.77\%$  similar, whereas Zn samples were  $91.87 \pm 3.43\%$  similar. Standard Reference Material for the Keweenaw cores was from Ultra Scientific Co (Natural Matrix Certified Reference Material "Metals on Soil/Sediment #4"). Recoveries (N = 15) were Cu  $90.01 \pm 11.56\%$ , Zn  $97.28 \pm 9.03\%$ , and Hg  $96.65 \pm 9.01\%$ . Replicate core samples (N = 16) gave the following similarity values: Cu  $90.35 \pm 5.77\%$ , Zn  $92.05 \pm 6.11\%$ , Hg  $91.12 \pm 4.46\%$ .

In the offshore Hg determinations, approximately 16% of all analyses were blanks, standard reference materials, and replicate extracts of samples. Based on the standard deviation of blanks, the detection limit was < 0.00489  $\mu\text{g/g}$  for the typical weight of sample extracted. All blanks were below the limit of detection for the instrument, whereas all sample results were above this limit. The mean percent relative difference for replicate extracts was 8.4%. Standard Reference Material 2704 was extracted with each set of microwave digested samples (NIST 1990). For the EPA lab, the acceptable recovery range was 80 to 120%. SRM 2704 recoveries ranged between 84 and 118%, with a mean of 104%. The certified concentration for mercury in SRM 2704 was 1.47  $\mu\text{g/g}$ , whereas the extracted amount was 1.53  $\mu\text{g/g}$ .

#### Inventory Calculations

It is assumed that post-depositional diagenetic remobilization of Cu, Zn, and Hg is small relative to the difference between anthropogenic and natural loadings. Anthropogenic copper inventories were calculated by determining the excess copper inventory above background over the length of the core:

$$C_a = \sum_i (C_t - C_b) M_i \quad (1)$$

where  $C_a$  = anthropogenic copper ( $\mu\text{g}/\text{cm}^2$ ) summed over depth ( $i$ , in cm),  $C_t$  = total copper concentration ( $\mu\text{g}/\text{g}$ ),  $C_b$  = background concentration ( $\mu\text{g}/\text{g}$ ), and  $M_i$  = total mass ( $\text{g}/\text{cm}^2$ ). The sediment accumulation rate for anthropogenic copper in recent sediments is:

$$R = C_i * M_i * 1/t \quad (2)$$

where  $R$  = net flux ( $\mu\text{g}/\text{cm}^2/\text{yr}$ ),  $C_i$  = inventory concentration ( $\mu\text{g}/\text{cm}^2$ ),  $t$  = accumulation duration (years). Deposition rates for 16 core sites were derived from literature values based on close-interval sectioned cores taken at the same sites.

$^{137}\text{Cs}$  and  $^{210}\text{Pb}$  dating (Robbins and Edgington 1975; Whitefish Bay core) and slime clay layers (Keweenaw cores) aided time-specific assignment of Cu and Hg increases (Kerfoot *et al.* 1994, Kerfoot and Robbins 1999). Sediment focusing, however, can redistribute sediment in a non-uniform manner, requiring corrections. In the NOAA 2 cm-sectioned cores,  $^{137}\text{Cs}$  inventories were used primarily to correct for sediment focusing, using an expected mean value of  $24.0 \text{ dpm}/\text{cm}^2$  derived from decay-corrected atmospheric deposition. That is,

$$\text{Focusing Correction} = R/F \quad (3)$$

where  $F$  = focusing factor = Observed/Expected  $^{137}\text{Cs}$  inventory.

### Cu/Zn Ratios and Cu Concentrations

To help trace nearshore patterns back to sources, Cu/Zn ratios and Cu concentrations were used. Prior Neutron Activation studies (Kerfoot and Robbins 1999) showed that the Cu/Zn ratio is a strong indicator of local mining perturbations. Cu/Zn ratios for stamp sand samples from the Gay, Isle Royale, and Point Mills stamp sand piles range between 10 and 67 for the  $< 1 \text{ mm}$  and 12 and 38 for the  $< 177 \text{ mm}$  size fraction. Copper is differentially enriched in copper ore lodes relative to Zn, and even more strongly enriched in the fine "slime clay" fraction of stamp sands, the fraction most easily dispersed from tailing piles into Lake Superior. Consequently, Cu/Zn ratios were inspected from published data on sediment samples and from inventory cores taken across the eastern Lake Superior basin.

To illustrate the association between the location

of stamp sand mills and copper in sediments (surficial Cu concentrations, anthropogenic inventories), values along the stretch of the Keweenaw Waterway were plotted, starting from the North Entry (km 0) to the South Entry (km 37). The values were compiled from literature records (Fitchko and Hutchinson 1975, Wright *et al.* 1975, Sypniewski 1977, Kraft and Sypniewski 1981, Malueg *et al.* 1984, Leddy 1973, Kerfoot *et al.* 1994). A Spline regression (Systat, Wilkinson 1989) was fit to the values.

### Michigamme Project Inland Lake Cores

As part of a regional investigation of trace metal contamination (Evans 1986), a Wildco KB 5.1 cm diameter gravity corer was used to obtain cores from seven lakes on or near the Keweenaw Peninsula. Only cores with a relatively undisturbed surface were selected for analysis. Cores for the Michigamme Project were extruded and sliced into 1 cm sections. Samples were analyzed at the MDNR laboratory, Lansing, following US EPA approved analytical methodologies. Data and core samples were made available to us as part of a 1995 Deer Lake Project.

## RESULTS

### Lake Superior Copper Inventories

The locations of coring sites across Lake Superior are indicated in Figure 1. Surface and background copper concentrations, maximum values, and anthropogenic inventories from individual sites are listed in Table 1. The text gives ninety-five percent confidence intervals for mean estimates.

After excluding cores whose lowest strata (20 cm depth) clearly had not reached background levels, it was found that background copper concentrations ranged from 21 to 75  $\mu\text{g}/\text{g}$  (mean  $\pm$  95%CL,  $60.9 \pm 7.0 \mu\text{g}/\text{g}$ , CV = 32%), whereas surface copper concentrations ranged from 47 to 281  $\mu\text{g}/\text{g}$  ( $164.3 \pm 22.1 \mu\text{g}/\text{g}$ ; CV = 37%). Surface Cu concentrations (Fig. 3) were lowest in the extreme western and eastern basins (Duluth Basin, Whitefish Bay) and highest in mid-lake and mid-eastern basin regions.

At shallow depths in the cores, the ratio of the Cu concentration peak to background values ranged from 1.6 to 8.9 ( $3.1 \pm 0.2$ , CV = 41%), indicating sizable anthropogenic inputs. The ratio of maximum copper to background concentration was lowest in the western basins (Duluth, Thunder Bay),

**TABLE 1.** Copper concentrations, inventories, and important ratios from the 1983 Lake Superior cores. Abbreviations in table heading correspond to: *bkg* = background concentrations; *Surf* = Surficial concentrations; *Max* = maximum concentrations; *S:B* = Surficial/Background ratio; *M:B* = Maximum/Background ratio; *Total* = total copper inventory; *Anth* = anthropogenic copper inventory; *FF* = Focusing Factor, calculated from cesium accumulation; *Corr Anth* = anthropogenic inventory corrected for sediment focusing. Units of measure are given under the measurements.

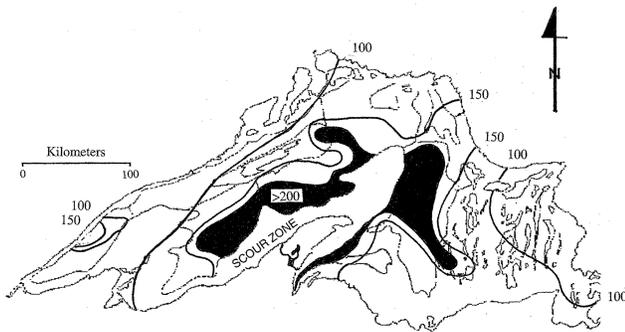
| Station | Bkg   | Sur                 | Max   | S:B | M:B | Total                  | Anth  | FF  | Corr. Anth             |
|---------|-------|---------------------|-------|-----|-----|------------------------|-------|-----|------------------------|
|         |       | ( $\mu\text{g/g}$ ) |       |     |     | ( $\mu\text{g/cm}^2$ ) |       |     | ( $\mu\text{g/cm}^2$ ) |
| EV11A   | 36.8  | 91.9                | 120.9 | 2.5 | 3.3 | 585.8                  | 308.3 | 3.0 | 102.8                  |
| SV45    | 61.7  | 204.4               | 204.4 | 3.3 | 3.3 | 510.4                  | 71.1  | 0.7 | 101.6                  |
| EV24    | 50.6  | 171.0               | 171.0 | 3.4 | 3.4 | 561.6                  | 108.6 | 0.6 | 181.0                  |
| SJE     | 59.1  | 174.0               | 174.0 | 2.9 | 2.9 | 449.1                  | 130.0 | 1.3 | 100.0                  |
| I7      | 20.6  | 47.3                | 184.2 | 2.3 | 8.9 | 652.7                  | 421.1 | 2.6 | 162.0                  |
| L42C    | 72.5  | 171.8               | 201.2 | 2.4 | 2.8 | 446.8                  | 90.1  | 0.7 | 128.7                  |
| B247    | 47.70 | 147.3               | 147.3 | 3.1 | 3.1 | 581.8                  | 94.3  | 1.0 | 94.3                   |
| EV23    | 40.1  | 147.9               | 147.9 | 3.7 | 3.7 | 318.0                  | 44.5  | 1.0 | 44.5                   |
| JAR     | 67.2  | 196.5               | 196.5 | 2.9 | 2.9 | 639.1                  | 116.8 | 1.1 | 106.2                  |
| PS21    | 49.9  | 81.4                | 81.4  | 1.6 | 1.6 | 570.0                  | 134.7 | 2.1 | 64.1                   |
| SV180   | 63.1  | 75.5                | 116.8 | 1.2 | 1.9 | 384.5                  | 46.6  | 0.5 | 93.2                   |
| EV8     | 60.0  | 109.7               | 123.0 | 1.8 | 2.1 | 394.2                  | 122.8 | 0.9 | 136.4                  |
| EV26A   | 60.1  | 213.9               | 226.8 | 3.6 | 3.8 | 240.5                  | 240.5 | 1.1 | 218.6                  |
| T46A    | 93.76 | 281.0               | 281.0 | 3.0 | 3.0 | 839.4                  | 383.8 | 2.0 | 191.9                  |
| L42A    | 77.4  | 270.6               | 270.6 | 3.5 | 3.5 | 644.5                  | 348.9 | 1.5 | 232.6                  |
| SV169   | 52.5  | 219.7               | 219.7 | 4.2 | 4.2 | 594.9                  | 153.2 | 0.6 | 255.3                  |
| PS16    | 66.8  | 196.8               | 196.8 | 2.9 | 2.9 | 500.7                  | 136.8 | 0.9 | 152.0                  |
| 25A     | 47.9  | 154.3               | 173.6 | 3.2 | 3.6 | 483.2                  | 266.1 | 2.2 | 121.0                  |
| SV42    | 65.9  | 215.1               | 225.5 | 3.3 | 3.4 | 531.1                  | 261.6 | 2.0 | 130.8                  |
| EV12    | 53.7  | 152.7               | 152.7 | 2.8 | 2.8 | 459.2                  | 96.9  | 0.9 | 107.7                  |
| SV43    | 61.7  | 213.9               | 236.2 | 3.5 | 3.8 | 660.6                  | 228.2 | 0.9 | 253.6                  |
| PS8     | 98.6  | 263.2               | 263.2 | 2.7 | 2.7 | 840.8                  | 167.8 | 0.9 | 186.4                  |
| SV157   | 55.0  | 143.5               | 143.5 | 2.6 | 2.6 | 535.2                  | 72.2  | 0.3 | 240.7                  |
| PS20    | 37.8  | 89.2                | 89.2  | 2.4 | 2.4 | 486.2                  | 151.5 | 1.7 | 89.1                   |
| EV21    | 45.9  | 153.9               | 170.9 | 3.4 | 3.7 | 446.3                  | 184.4 | 0.8 | 230.5                  |
| EV4     | 52.8  | 95.8                | 111.1 | 1.8 | 2.1 | 660.7                  | 94.7  | 1.1 | 86.1                   |
| KB      | 113.4 | 227.5               | 335.5 | 2.0 | 3.0 | 1,450.8                | 779.8 | 4.2 | 185.7                  |
| G18     | 60.5  | 177.1               | 177.1 | 2.9 | 2.9 | 402.9                  | 121.3 | 1.2 | 101.1                  |
| S24     | 69.2  | 142.8               | 145.9 | 2.1 | 2.1 | 513.5                  | 211.6 | 3.1 | 68.3                   |
| EV13    | 86.0  | 99.6                | 112.6 | 1.2 | 1.3 | 542.0                  | 20.8  | 3.6 | 5.8                    |

but exceeded 3.0 at several mid-lake and eastern basin sites.

Total copper inventories for cores were high ( $563 \pm 76 \mu\text{g/cm}^2$ ; CV = 37%), a reflection of basin ore sources naturally scoured along shorelines and seamounts as well as anthropogenic inputs. Anthropogenic inventories uncorrected for focusing (Fig. 3) varied from 20 to  $780 \mu\text{g/cm}^2$  ( $187 \pm 54 \mu\text{g/cm}^2$ ; CV = 81%). In general, inventories were highest in mid-lake and deep-water eastern depositional basins. Exceptionally high values came from sites near mining activity (I7, Silver Bay taconite discharges into the Duluth Basin; KB, Gay stamp mill discharges into Keweenaw Bay).

Based on  $^{137}\text{Cs}$  inventories, focusing factors ranged from 0.4 to 4.2 ( $1.46 \pm 0.36$ ), suggesting a broad range of erosional (< 1.0) and excess depositional (> 1.0) regimes. The relatively large mean value underscores the deep scour zone of the high-energy Lake Superior environment, moving fine-grained sediment off shelves less than 50 m into deeper waters. Overall, focusing corrections lowered the inventory mean value and decreased site variance ( $144 \pm 22 \mu\text{g/cm}^2$ ; CV = 42%). Corrected inventory values emphasized the Cu-enriched region around the Keweenaw Peninsula (Fig. 3, Table 2).

At deep-water stations, several of the cores had



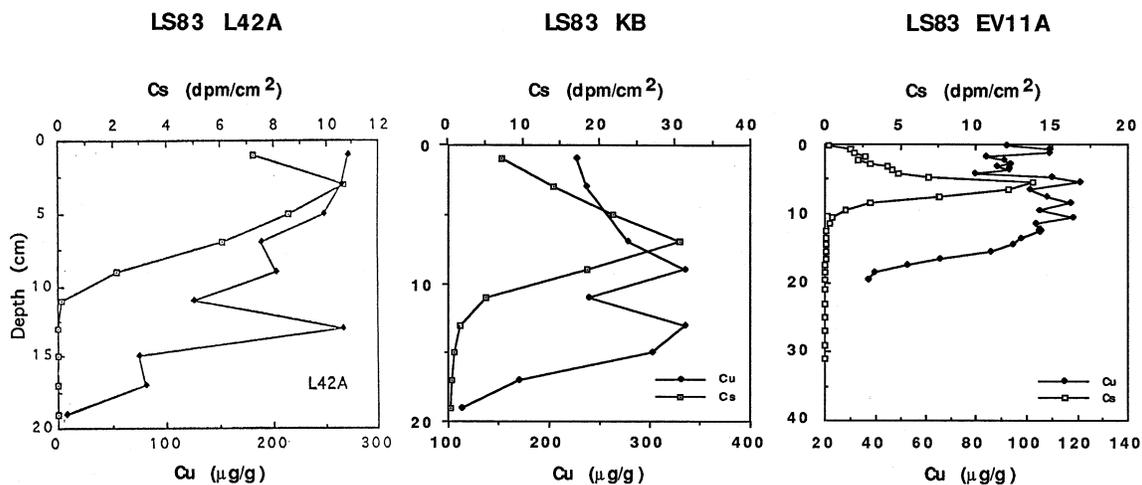
**FIG. 3.** Copper in Lake Superior sediments: general patterns for corrected anthropogenic inventories. Dark region includes inventories usually  $> 200 \mu\text{g}/\text{cm}^2$ , with declining values away from the Keweenaw Peninsula, excepting the Silver Bay taconite discharges in the Duluth basin.

very low deposition rates, making it impossible to resolve fluctuations in copper concentrations over decade intervals. However, thirteen of the thirty cores (43%) from modest to high depositional environments exhibited buried maxima, eight having pronounced maxima (KB and EV11A, Fig. 4). Cores with high inventories where an increase in Cu over background probably occurred before 20 cm depth include cores KB and T46A. Cores with an increase in Cu over background at 20 to 15 cm depth were S-24; 15 to 10 cm depth, SV-42, SV-43; 10 to 5 cm depth, SV 180, SJE, PS-8; and 5 to 0 cm depth, SV 45, SV 169, EV 24. The sites with buried maxima are scattered geographically, suggesting

that this phenomenon is widespread in Lake Superior.

Within the variables measured at each location, there was only one strong correlation, between maximum copper concentration and corrected anthropogenic copper inventory (Spearman Corr = 0.728,  $P < 0.001$ ). The latter relationship is somewhat intuitive, as higher concentrations lead to higher inventories. There are other modest correlations, one between background and surface copper concentrations (Spearman Corr = 0.592;  $P < 0.001$ ), and the other between surface to background ratios and corrected anthropogenic inventories (0.530;  $P < 0.003$ ). The first moderate correlation may reflect scour of ore deposits, whereas the second merely indicates that historical disturbances persist in surface strata. The Spearman Rank Order correlation between uncorrected and corrected anthropogenic inventories is only modest (0.505;  $P < 0.005$ ), underscoring that focusing correction fundamentally alters the ranking of sites.

Examples of buried Cu maxima and corresponding Cs profiles (Fig. 4) are illustrated from the Caribou Basin (L42A), Keweenaw Bay (KB), and Whitefish Bay (EV11A). All three cores show initial increases in Cu concentrations dating before World War II, probably from 1900 to the 1920s, the latter two cores having a well-defined later 1960 Cs peak. With the exception of an early fluctuation, the Caribou Basin core (L42A) shows Cu increasing early from  $70 \mu\text{g}/\text{g}$  to eventually reach  $270 \mu\text{g}/\text{g}$ . The Keweenaw Bay core (KB) missed background



**FIG. 4.** Total Cu and  $^{137}\text{Cs}$  profiles for several Lake Superior sediment cores (EV11A, Whitefish Bay; L42A, Caribou basin; KB, Keweenaw basin).

**TABLE 2. Summary statistics for 1983 Lake Superior core variables and copper inventories. Concentrations in  $\mu\text{g/g}$  and inventories in  $\mu\text{g/cm}^2$ .**

| Variable                  | N  | Mean  | SE   | SD   | CV |
|---------------------------|----|-------|------|------|----|
| Background Cu Conc        | 30 | 60.9  | 3.5  | 19.2 | 31 |
| Surface Cu Conc           | 30 | 164.3 | 11.1 | 60.5 | 37 |
| Surface: Background Conc  | 30 | 2.74  | 0.14 | 0.75 | 27 |
| Maximum Cu Conc           | 30 | 180   | 11   | 60   | 33 |
| Maximum: Background Conc  | 30 | 3.12  | 0.24 | 1.29 | 41 |
| Total Cu Inventory        | 30 | 563   | 38   | 206  | 37 |
| Anthropogenic Inventory   | 30 | 187   | 27   | 151  | 81 |
| Focusing Factor           | 30 | 1.46  | 0.18 | 1.00 | 68 |
| Corrected Anth. Inventory | 30 | 144   | 12   | 67   | 47 |

strata as bottom (20-cm) Cu concentrations increase beyond 100  $\mu\text{g/g}$  upwards and peak at over 300  $\mu\text{g/g}$ , then decline below 230  $\mu\text{g/g}$  in surface strata. The Cs peak occurs in this core after the decline in Cu. In Whitefish Bay (EV11A), Cu concentrations are much lower at 20 cm depth, around 40  $\mu\text{g/g}$ , increase to a value of 120  $\mu\text{g/g}$  initially, then fluctuate between 80 and 110  $\mu\text{g/g}$ . In this case the 1960 Cs peak occurs at the beginning of the decline in Cu concentrations. High Cu inventories near the Marathon Basin (T46A, 25A), Thunder Bay (S24), Keweenaw Bay (KB), and Silver Bay (I7, SV180) correspond to elevated mining activities in those regions. Core I7 reflects local inputs of taconite tailings from the Reserve Mining operation at Silver Bay, MN (Rossmann 1999).

#### Site Copper Fluxes and Loading

Site-specific sedimentation rates for sixteen locations were multiplied by copper concentrations to determine site-specific surficial Cu fluxes (Table 3). Three sites gave exceptionally high values: I7 in the Duluth Basin (19.9  $\mu\text{g/cm}^2/\text{yr}$ ); KB in the Keweenaw Bay Trough (9.9  $\mu\text{g/cm}^2/\text{yr}$ ); and T46A in the Marathon Basin (7.2  $\mu\text{g/cm}^2/\text{yr}$ ). Based on all sixteen sites, the mean lake-wide loading estimate for Cu is  $5.0 \pm 2.5 \mu\text{g/cm}^2/\text{yr}$ . If the three extremely high deposition sites are removed, the mean loading estimate is reduced to  $3.4 \pm 1.2 \mu\text{g/cm}^2/\text{yr}$ .

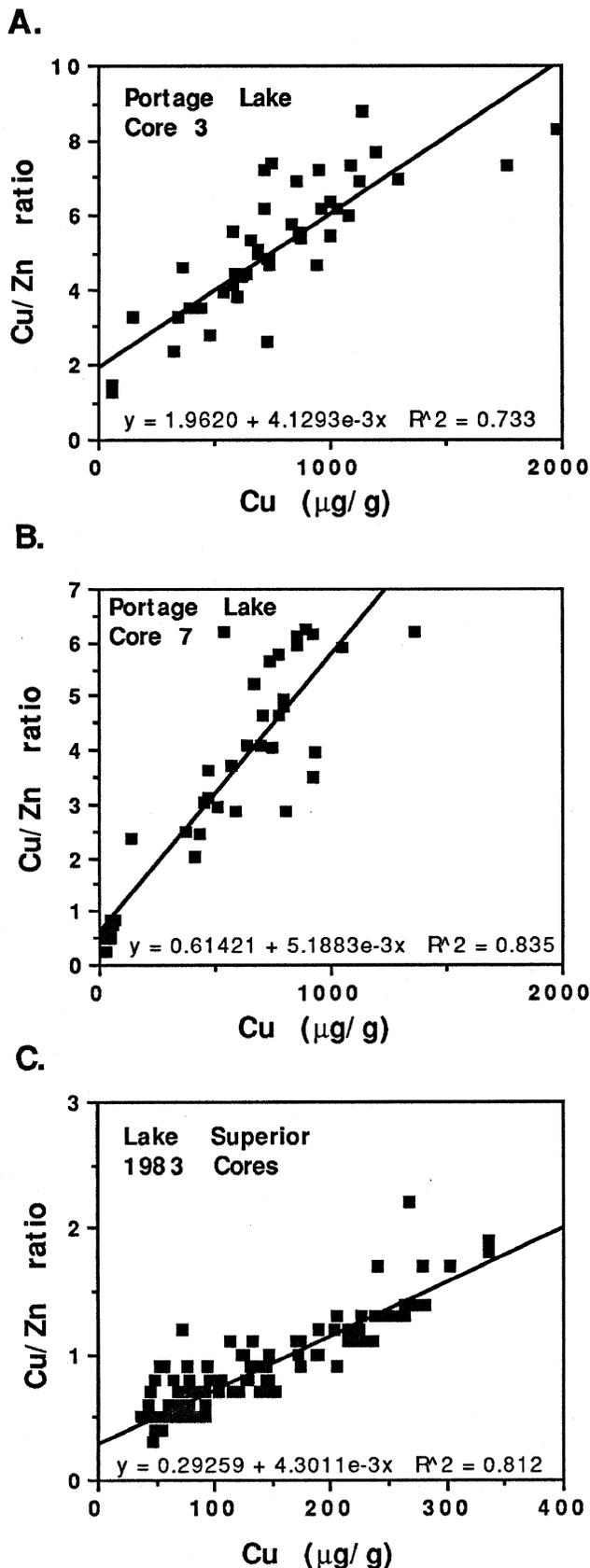
#### Evidence for Mining Impacts: Cu/Zn Ratios

Copper is normally less abundant than Zn in lake sediments, due to the constitution of elements in bedrock, the greater solubility of Zn, and higher concentrations of Zn relative to Cu in living matter.

Neutron activation studies (Kerfoot and Robbins 1999) revealed that a high abundance of Cu relative to Zn is characteristic of native copper ores. Thus the ratio of the two elements provides a good indicator of local mining influences around the Keweenaw Peninsula. Ratios are very high in ores and stamp sands, and remained moderately high in lakes and along shorelines that received stamp sand clay particles (Fig. 5, Table 4).

Table 4 lists the 95% confidence limits for Cu/Zn ratios run on stamp sand samples and surficial sediments from a variety of sites: Portage Lake, the rest of the Keweenaw Waterway, Lake Superior, and inland lakes. Copper to zinc ratios ranged between 10 and 67 (mean 23.4) in the so-called slime clay fraction of stamp sands, between 4 and 15 (mean 10.0) in Torch Lake sediments and 1 and 24 (mean 9.0) in Portage Lake surface and deeper mining era sediments. A review of published sediment values shows that Cu/Zn ratios are higher in the southern sites of the eastern Lake Superior Basin, and lower in the northern sites. Southern Lake Superior sites had a mean Cu/Zn ratio of 1.95 at -5 cm depth, decreasing to 1.64 in surface sediments. Northern Lake Superior sites had a mean of 1.06 at -5 cm depth, decreasing to 0.92 in surface sediments. Although the mean differences seem slight, they are significant ( $P < .05$ ; Table 4). Inland lakes had a mean Cu/Zn ratio of 0.79.

Not all local environments showed mining impacts. At the South Entry of the Keweenaw Peninsula, wetland regions of the waterway apparently were protected from slime clay-laden mining discharges by the large volume of water discharged by the Sturgeon River. In this region, zinc dominated, giving Cu/Zn ratios between 0.3 and 0.5



(mean 0.4), similar to data from undisturbed inland habitats.

There are high correlations between Cu concentration and the Cu/Zn ratio in Portage Lake cores and in the 1983 Lake Superior cores (Figs. 5a–c). This relationship seems unique to Lake Superior among the Laurentian Great Lakes and possibly relates directly to mining activity and naturally scoured ore deposits. The high correlations between Cu concentration and the Cu/Zn ratio suggest that the fine fraction from tailing discharges (slime clay fraction) provided a source of fine, copper-rich particulate material to at least nearshore sediments, if not deeper offshore stations. Regression coefficients are similar, suggesting a simple dispersal and dilution relationship for dispersed clay-sized particles. At deep-water sites, Cu cycling through various dissolved states and through food chains, which favor Zn relative to Cu, should correct the mining-related imbalance with time, returning the sediment ratios to more typical values. Transformation of Cu from slime clay particle-bound forms into soluble forms capable of cycling through deep-water food chains is probably an important process currently operating in Lake Superior offshore waters. The presence of a buried Cu/Zn maximum in the sediment profile signals either that the recovery process is underway or that remobilized copper is plating out on the redox horizon (McKey et al 1989) perhaps in proportion to increased historical inventories.

#### Tracing Enrichments Back to Sources: Surface Cu Patterns and Copper/Mercury Profiles

Three different types of copper and mercury sediment profiles (Fig. 6) are distinguished. One pattern, primarily found far offshore at low deposition, deep-water sites, exhibits surface increases in copper and mercury concentrations, with low invento-

**FIG. 5.** Cu/Zn ratios plotted against Cu concentrations for: A) various depths of Portage Lake core #3, central basin, B) various depths of Portage Lake core #7, near Sturgeon River discharge; C) various depths of 1983 Lake Superior inventory cores. Least-square regression equations fit to points and coefficients of determination ( $R^2$ ) given at bottom of graphs. Note that regression slopes are similar over wide range of absolute values.

**TABLE 3. Estimated sediment flux and calculated Cu flux at sixteen lake Superior sampling locations. Sources for sediment flux estimates listed by author.**

| Station | Sed. Flux (g/cm <sup>2</sup> /yr) | Cu Conc. (µg/g) | Flux (µg/cm <sup>2</sup> /yr) | Source   |
|---------|-----------------------------------|-----------------|-------------------------------|----------|
| EV24    | 0.013                             | 171.0           | 2.22                          | Klump    |
| SJE     | 0.018                             | 174.0           | 3.13                          | Klump    |
| I7      | 0.42                              | 47.3            | 19.9                          | Rossmann |
| B247    | 0.017                             | 147.3           | 2.50                          | Bruland  |
| EV23    | 0.014                             | 147.9           | 2.07                          | Evans    |
| EV8     | 0.022                             | 109.7           | 2.41                          | Evans    |
| EV26A   | 0.022                             | 213.9           | 4.71                          | Evans    |
| T46A    | 0.0255                            | 281.0           | 7.17                          | Kemp     |
| 25A     | 0.0155                            | 154.3           | 2.39                          | Kemp     |
| EV12    | 0.016                             | 152.7           | 2.44                          | Evans    |
| PS20    | 0.08                              | 89.0            | 7.12                          | Klump    |
| EV21    | 0.007                             | 153.9           | 1.08                          | Evans    |
| EV4     | 0.016                             | 95.8            | 1.53                          | Evans    |
| KB      | 0.0435                            | 227.5           | 9.90                          | Kemp     |
| S24     | 0.046                             | 142.8           | 6.57                          | Kemp     |
| EV13    | 0.053                             | 99.6            | 5.28                          | Evans    |

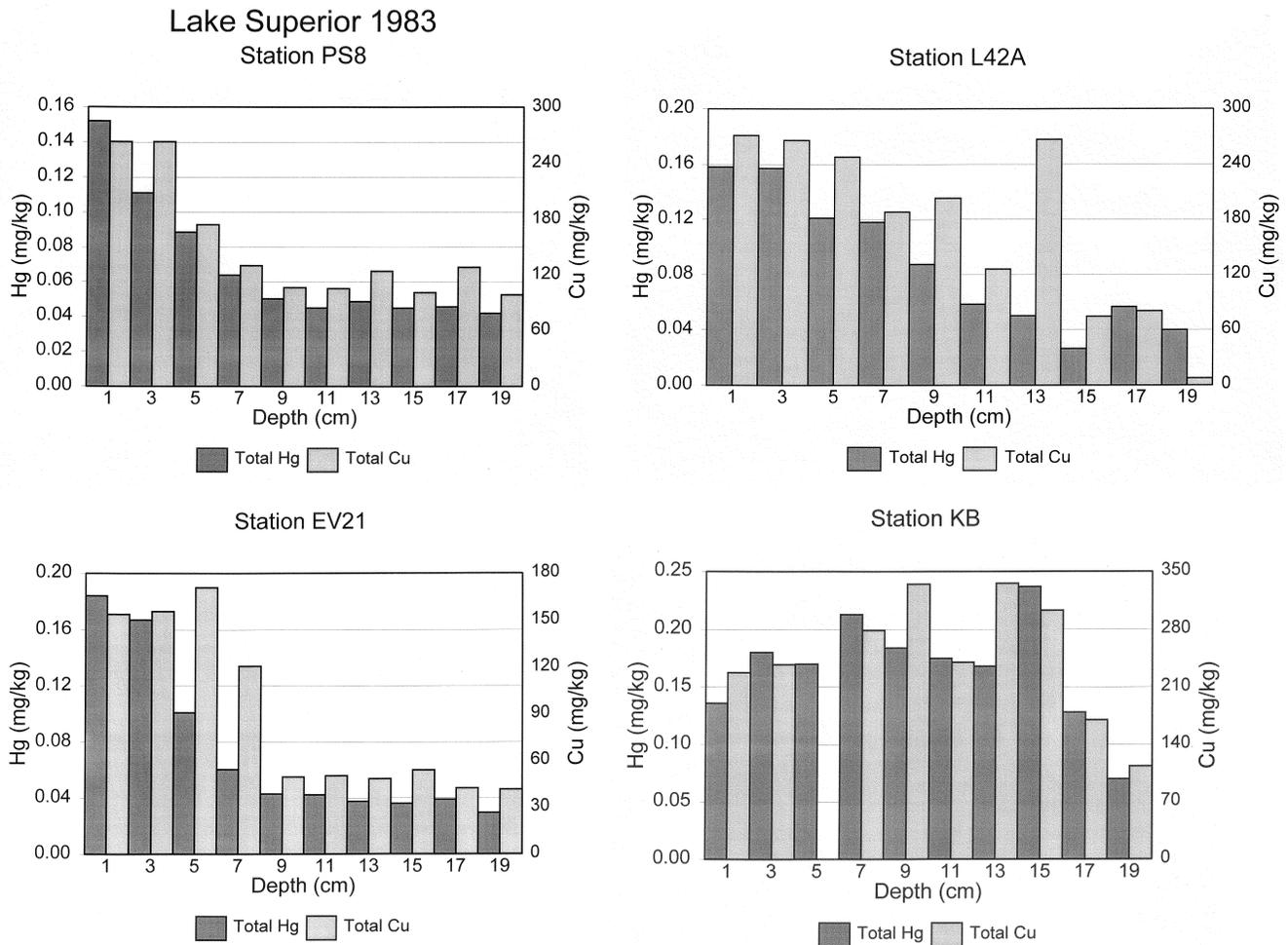
ries suggestive of atmospheric sources or an active floc exchange layer (stations PS 8 and EV 21). A second pattern, characteristic of intermediate deposition regimes at deep-water sites, features early increases in copper concentrations, corresponding to turn-of-the-century mining discharges, followed later by an increase in mercury concentrations which peaks near the surface (station L 42A). A third pattern, present at high depositional sites strongly influenced by coastal currents, shows simultaneous early rises of copper and mercury concentrations with examples of buried maxima and high inventories (station KB).

Several regional and local sources of copper and mercury occur within the basin. Natural erosion of metal-rich geologic formations historically elevated metal fluxes relative to other Great Lakes watersheds. Mining of base metal deposits (gold, silver, copper) accelerated these high background fluxes. Historically, mercury associated with mining came from three principal sources: 1) imported into the basin for metal extraction and assay procedures (gold amalgamation technique; ferrous iron assay), 2) found as a natural amalgam in silver-rich copper and gold deposits, becoming locally enriched in tailings deposits, and 3) discharged from smelters that processed copper enriched in silver, spreading metal-enriched plumes across regional watersheds and drainage systems.

Indirect evidence for the natural amalgam hypothesis comes from a significant association be-

tween mercury and silver concentrations at several sediment core sites. It is hard to believe that such a pattern could arise from long-distance deposition of mercury, since silver has restricted atmospheric mobility. At coring site T-46A, the concentration of Hg is high (mean 0.086 µg/g) relative to background levels, ranging between 0.045 and 0.150 µg/g. Silver is also high at this site (mean 0.453 µg/g), ranging between 0.327 and 0.607 µg/g. The correlation between Hg and Ag is significant ( $r = 0.671$ ;  $0.05 > P > 0.01$ ). Concentrations of both Hg and Ag are also high at PS-8 (Hg mean 0.071 µg/g, range 0.045 to 0.155; Ag mean 0.321 µg/g; range 0.258 to 0.412) and also significantly correlated ( $r = 0.810$ ,  $0.01 > P > 0.001$ ,  $N = 10$ ). Several stations off the Keweenaw Peninsula also have significant Hg:Ag correlations (L-42C, Ag mean 0.087 µg/g,  $r = 0.951$ ,  $P < 0.001$ ,  $N = 10$ ; SJE, Ag mean 0.18 µg/g,  $r = 0.642$ ,  $P < 0.05$ ,  $N = 10$ ; SV-169, Ag mean 0.174 µg/g,  $r = 0.899$ ,  $P < 0.001$ ,  $N = 10$ ).

Contributions from stamp mills (terrestrial inputs) are relatively easy to trace back to shoreline sources, using high Cu concentrations, Cu/Zn ratios, or ore elemental composition (Kerfoot and Robbins 1999). Identifying contributions from smelters (terrestrial slag dumps, atmospheric plumes) is more difficult. Stamp sand discharge sites are well known historically (Kerfoot *et al.* 1994) and easily marked by shoreline piles, yet smelting operations in the Keweenaw Region also stretched across the entire peninsula, were generally



**FIG. 6.** Concentration profiles for copper and mercury from 1983 Lake Superior sediment cores. Stations PS8 and EV21 are from the center of Lake Superior, east of Isle Royale, whereas L42A is just north of the path of the Keweenaw Current and KB is from Keweenaw Bay. Sampling sites are plotted in Figure 1.

located near water for ease of finished ingot shipment, and produced plumes that blanketed downwind watersheds (Fig. 2).

For example, surficial copper concentrations along the Keweenaw Waterway peak near locations of stamp mills (Fig. 7). Concentrations start at relatively high values, 100 to 600  $\mu\text{g/g}$ , near the North Entry due to shoreline reworking of stamp sands discharged from the five mills at Freda and Redridge. Values increase to extremely high levels, 1,600 to 2,400  $\mu\text{g/g}$ , near the central Houghton and Hancock mill sites, then decline to very low values, 30 to 40  $\mu\text{g/g}$ , near the South Entry. Sediment core samples taken from Keweenaw Bay and from the Keweenaw Waterway near stamp mill sites show high concentrations for Cu and Hg and correlated

inventories (Fig. 8, Table 5). Figure 8 illustrates two examples of sediment core profiles, one from L'Anse Bay (near the Mass and Michigan Mill discharges) and one from Portage Lake (receiving discharges from the Franklin and Centennial Mills at Point Mills, Isle Royale Mill east of Houghton). Major increases in Cu concentrations above background levels (20 to 40  $\mu\text{g/g}$ ) in both cores signal the onset of turn-of-the-century stamp mill discharges (Kerfoot *et al.* 1994, Kerfoot and Robbins 1999). However, these cores also clearly show an increase in Hg concentrations that begins around the time of the initial Cu increase. In both cases there is evidence for a buried maximum, although peak Hg concentrations are less in L'Anse Bay (0.140  $\mu\text{g/g}$ ) than in Portage Lake (0.800  $\mu\text{g/g}$ ), re-

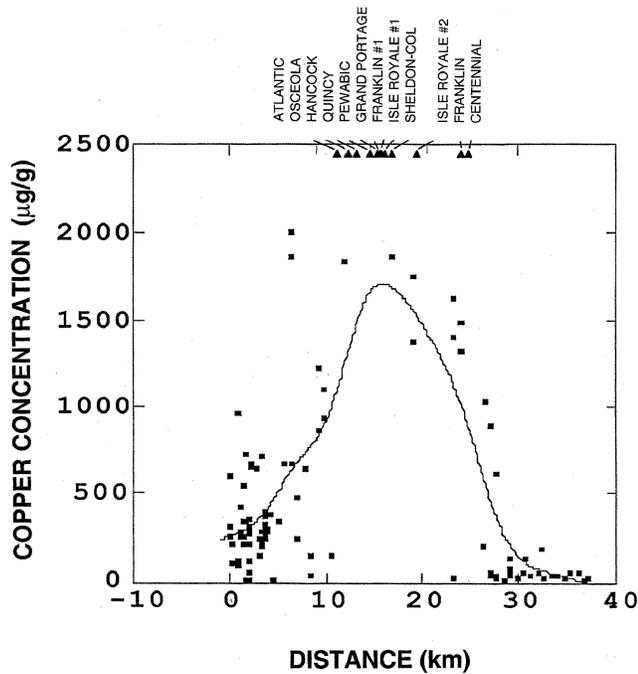
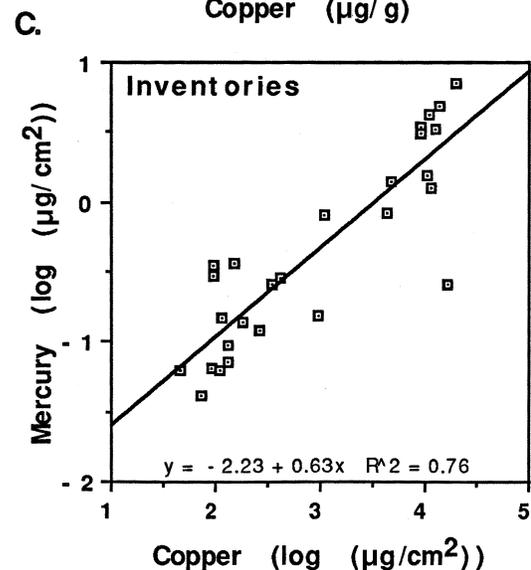
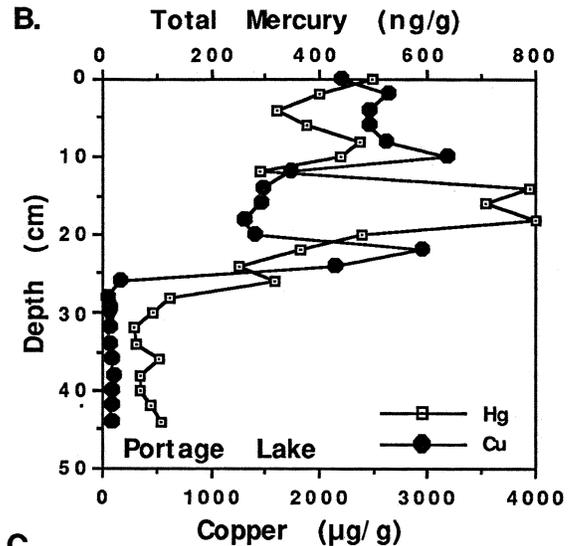
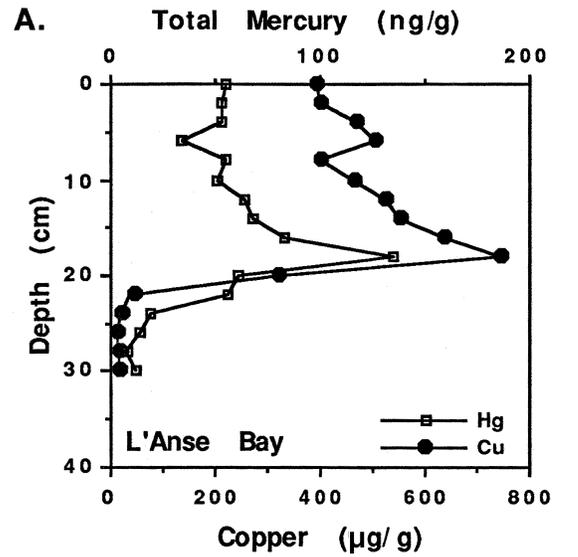


FIG. 7. Transect along the Keweenaw Waterway, moving from the North Entry (km 0) to the South Entry (km 37), illustrating how a) surface copper concentrations and b) copper inventories peak near the location of stamp mills. A spline regression fit traces the general mean trend of surface copper concentration.

lated to total stamp mill discharges. Copper and mercury inventories for the 36 total cores are highly correlated among sites ( $r = .874$ , with the one outlier), again reflecting a strong association with stamp mill discharges.

The core studies reported here are the first to document high mercury concentrations in Keweenaw Bay and Waterway deep sediments and to associate these patterns with mining activity. Direct evidence for the natural amalgam hypothesis comes from analyzing copper ore samples from several mine sites, both chunks of copper from poor rock piles and museum voucher samples. For example, the Isle Royale Mine, one of the three large opera-

FIG. 8. Copper and mercury inventories for Keweenaw Waterway and Keweenaw Bay (L'Anse Bay portion) sites. Selected examples from A) Portage Lake and B) L'Anse Bay; C) values from entire set of 22 cores (Table 5).



**TABLE 4.** Mean Cu/Zn ratios for surface sediments at various locations around the eastern Lake Superior basin, with sample sizes (N), standard errors (SE), coefficients of variation (CV, expressed as % mean), standard deviations (SD), and 95% confidence intervals for mean estimates (95% CL). Northern and southern Lake Superior samples broken into surface (s) and five centimeters depth (5). Lake Superior sources include Helmke et al. 1977; Mothersill and Fund 1972; Kemp et al. 1978; Nebrija 1979; whereas Keweenaw Waterway and Portage Lake include Kerfoot et al. 1994; Kerfoot and Robbins 1999; Leddy 1986; Malueg et al. 1984; and Wright et al. 193, 1975.

| Site                 | N   | Mean  | (SD)    | CV   | SE   | 95% CL |
|----------------------|-----|-------|---------|------|------|--------|
| Stamp Sands          | 19  | 23.40 | (15.83) | 68%  | 3.63 | ± 7.62 |
| Torch Lake           | 21  | 9.97  | (2.53)  | 55%  | 0.55 | ± 1.15 |
| Portage Lake         | 16  | 9.00  | (5.33)  | 133% | 1.33 | ± 2.83 |
| Keweenaw Waterway    | 217 | 5.49  | (4.06)  | 28%  | 0.28 | ± 0.45 |
| S. Lake Superior (s) | 192 | 1.64  | (1.45)  | 10%  | 0.10 | ± 0.20 |
| S. Lake Superior (5) | 106 | 1.95  | (1.66)  | 16%  | 0.16 | ± 0.32 |
| N. Lake Superior (s) | 74  | 0.92  | (0.58)  | 7%   | 0.07 | ± 0.14 |
| N. Lake Superior (5) | 33  | 1.06  | (0.76)  | 13%  | 0.13 | ± 0.26 |
| Inland Lakes         | 45  | 0.79  | (0.71)  | 11%  | 0.11 | ± 0.22 |
| South Portage        | 5   | 0.37  | (0.07)  | 3%   | 0.03 | ± 0.08 |

tions that contributed to Portage Lake stamp mill discharges, had total mercury concentrations that ranged between 0.842 and 4.388 µg/g (N = 4, mean 2.445 µg/g) in copper samples. Mercury concentrations in copper samples from the thirteen mine sites ranged between 0.761 and 10.850 µg/g (N = 27, mean 4.884 ± 1.234 µg/g).

#### Michigamme Project Lakes

The Michigamme data set (Evans 1988) allowed checks on highly localized signatures of mining activity, including stamp mills, smelter plumes, and assay laboratory discharges. Anthropogenic inventories for Cu from various small lakes are presented in Table 6. Gratiot Lake is located near naturally rich Cu ore bodies as reflected in the high background concentrations, but was never a site of mining. The Gratiot Lake copper anthropogenic inventory is low, despite the proximity to ore bodies. Lakes Emily and Medora are also distant from mining activities. However, Lac LaBelle was the site of two small stamp mills that operated between 1864 and 1889, as well as a short-lived smelting operation in the 1860s. Deer Lake (a recognized Area of Concern), Ishpeming, is the site of the Ropes Gold Mine, an operation which historically utilized mercury amalgamation. Deer Lake also received ionic mercury discharged from a mining laboratory in Negaunee during 1929 to 1981, generated from a ferrous iron assay technique.

Because high copper concentrations, high Cu/Zn

ratios, and high mercury concentrations are characteristic of milling sites, the isolated Lac LaBelle core profiles were used as an independent check on stamp sand discharges (Fig. 9). Lac LaBelle turned out to have the highest Cu inventories of the seven lakes, high Cu/Zn concentration ratios, and high sediment Hg concentrations. However, concentrations of Hg in Deer Lake sediments were so high that they required a scale shift (Fig. 10). Although historic smelter plume impacts on the Keweenaw Peninsula watershed have not been thoroughly investigated, cores taken downwind of smelter plumes, in Rice Lake (Superior Smelter, Dollar Bay) and Lakes Emily and Roland (east of the White Pine Smelter) also suggest atmospheric trace metal (Cu,Hg) inputs from smelter plumes (Fig. 10).

#### DISCUSSION

In one of the few early studies of copper from Lake Superior sediments, Kemp *et al.* (1978) attributed high anthropogenic copper loadings across the lake basin to mining activities, i.e. local sources. Curiously, Kemp *et al.* (1978) also stated that atmospheric inputs contributed 26.5% of total copper loading, suggesting major, perhaps long-distance, atmospheric inputs. Given the great areal expanse of Lake Superior, the two concepts are not incompatible. That is, depositional basins far offshore could be heavily influenced by atmospheric inputs, at the same time that nearshore discharges gradu-

**TABLE 5. Anthropogenic copper and mercury inventories from Keweenaw Peninsula region (Keweenaw Waterway, L'Anse Bay) and offshore Lake Superior coring sites. These inventories are the data plotted in Figure 8c.**

| Region                                | Anthropogenic Inventories            |                                     |
|---------------------------------------|--------------------------------------|-------------------------------------|
|                                       | Copper ( $\mu\text{g}/\text{cm}^2$ ) | Mercury ( $\text{ng}/\text{cm}^2$ ) |
| A. Keenenaw Waterway                  |                                      |                                     |
| North Portage Arm                     | 16,509                               | 5,348                               |
| Off Dollar Bay-1                      | 14,568                               | 4,161                               |
| Off Dollar Bay-2                      | 4,606                                | 882                                 |
| Portage Lake Proper-1                 | 5,405                                | 3,093                               |
| Portage Lake Proper-2                 | 7,877                                | 3,680                               |
| Portage Lake Proper-3                 | 4,536                                | 1,881                               |
| Deep Hole-Portage Lake                | 6,559                                | 3,070                               |
| Off Isle Royale SS Pile               | 10,998                               | 4,939                               |
| South Portage Lake                    | 4,800                                | 3,539                               |
| Lepisto Marine                        | 11,251                               | 1,022                               |
| North of Lamarinde Shoal              | 9,213                                | 3,049                               |
| South of Lamarinde Shoal              | 5,805                                | 3,032                               |
| New Coast Guard Station               | 20,163                               | 7,929                               |
| Pike Bay                              | 1,081                                | 923                                 |
| Hancock                               | 13,371                               | 6,278                               |
| Coles Creek                           | 12,514                               | 2,979                               |
| Highpoint Bay                         | 6,912                                | 261                                 |
| Oskar Bay                             | 4,417                                | 565                                 |
| Osmar Plat                            | 10,481                               | 1,183                               |
| B. L'Anse Bay Portion of Keweenaw Bay |                                      |                                     |
| L'Anse Bay-1A                         | 2,315                                | 444                                 |
| L'Anse Bay-1B                         | 2,968                                | 329                                 |
| L'Anse Bay-2                          | 2,711                                | 426                                 |
| C. Lake Superior Series               |                                      |                                     |
| B-247                                 | 94                                   | 352                                 |
| EV-4                                  | 95                                   | 291                                 |
| EV-21                                 | 184                                  | 139                                 |
| EV-24                                 | 109                                  | 63                                  |
| I7                                    | 421                                  | 288                                 |
| JAR                                   | 117                                  | 147                                 |
| L42A                                  | 349                                  | 253                                 |
| L42C                                  | 90                                   | 65                                  |
| SJE                                   | 130                                  | 96                                  |
| SV-42                                 | 262                                  | 122                                 |
| SV-157                                | 72                                   | 41                                  |
| SV-169                                | 153                                  | 72                                  |
| SV-180                                | 47                                   | 62                                  |
| T-46A                                 | 944                                  | 151                                 |

ally work their way toward the center of Lake Superior with appreciable time lags.

Some of the Lake Superior core estimates agree closely with published values, whereas others show notable departures. Background copper concentrations from the 1983 cores (range 21 to 75  $\mu\text{g}/\text{g}$ , mean  $60.9 \pm 7.0$   $\mu\text{g}/\text{g}$ ) are similar to values reported

by previous workers (Nussman 1965, mean 71; Mudroch *et al.* 1988, 30 to 84; Kemp *et al.* 1978, 30 to 84; Kolak *et al.* 1998, mean 57). Surface copper concentrations (47 to 281  $\mu\text{g}/\text{g}$ , mean  $164.3 \pm 22.1$ ) fall within Nussman's (1965) reported range (19 to 691  $\mu\text{g}/\text{g}$ ; mean surficial 230), although the mean value reported here is lower, perhaps reflect-

**TABLE 6.** Copper concentrations and inventories in inland lakes, taken during 1988 as part of the Michigamme project. (Bkg = background concentrations; Surf = Surficial concentrations; max = maximum concentrations; S:B = Surficial/Background ratio; M:B = Maximum/Background ratio; Anth = total anthropogenic copper accumulation)

| Station      | Bkg    | Sur | Max | S:B  | M:B  | Anth                  |
|--------------|--------|-----|-----|------|------|-----------------------|
|              | (µg/g) |     |     |      |      | (µg/cm <sup>2</sup> ) |
| Gratiot Lake | 60.3   | 64  | 64  | 1.06 | 1.06 | 1.6                   |
| Lake Emily   | 25.7   | 140 | 140 | 5.45 | 5.45 | 75.0                  |
| Lake Medora  | 30.7   | 52  | 52  | 1.70 | 1.70 | 24.7                  |
| Rice Lake    | 25.7   | 174 | 178 | 6.78 | 6.93 | 221.4                 |
| Lake Roland  | 17.3   | 78  | 78  | 4.47 | 4.47 | 32.2                  |
| Lac LaBelle  | 52.3   | 380 | 410 | 7.26 | 7.83 | 1,193.4               |
| Deer Lake    | 48     | 210 | 220 | 4.38 | 4.58 | 703.4                 |

ing progressive recovery. The surface values generally fall within other reported values (Mudroch *et al.* 1988, range 113 to 300 µg/g; Kemp *et al.* range 113 to 213), but are higher than Kolak *et al.*'s range of 75 to 185 µg/g. The enrichment factor for copper (surface/background),  $2.74 \pm 0.28$ , is higher than the estimate obtained by Kemp *et al.* (1978; range 0.8–2.8, mean 1.88). The average background concentration of copper in Lake Superior cores is 1.5–2× higher than samples from other Great Lakes sediments, agreeing with the estimates of Mudroch *et al.* (1988).

### Atmospheric Component

Determining the relative contributions from atmospheric or terrestrial sources accurately is difficult. The controversy over atmospheric contributions demands attention, because of large uncertainties associated with overall cycling and the vast areal extent of Lake Superior. There are several ways to estimate atmospheric inputs of copper: 1) by obtaining sediment cores from isolated kettlehole lakes not subject to weathered bedrock or mining inputs, 2) by directly measuring atmospheric deposition at atmospheric monitoring stations, or 3) by using stable isotope techniques. None of these methods has been extensively employed in the Lake Superior basin, yet all are potentially applicable.

Kemp *et al.*'s estimated values for the atmospheric loading contribution came from two different sources, sediment core inventories (six cores) and tables of atmospheric deposition values from an International Joint Commission report (IJC 1977). An-

thropogenic loadings of copper to Lake Superior from Kemp *et al.*'s sediment cores averaged 3.8 µg/cm<sup>2</sup>/yr, whereas natural (background) loading averaged 2.1 µg/cm<sup>2</sup>/yr, giving a total flux of 5.9 µg/cm<sup>2</sup>/yr. After correction for the depositional basin size, anthropogenic loading was estimated as 66.3% of the total accumulation. The IJC report (1977) lists atmospheric inputs as 370 tonnes/yr and terrestrial inputs as 1,025 tonnes/yr. Using the IJC value for lake surface area,  $370 \times 10^{12}$  µg Cu were deposited over  $82,103 \times 10^{10}$  cm<sup>2</sup>, giving an estimated atmospheric flux of 0.45 µg Cu/cm<sup>2</sup>/yr. Dividing the latter value by the total estimated loading, 5.9 µg/cm<sup>2</sup>/yr, gives 7.6%, not the 26.5% claimed by Kemp *et al.* (1978). Correction of this calculation removes the ambiguity inherent in the original claims and emphasizes the terrestrial inputs.

Another estimate of atmospheric loading can be derived from a single nearshore site (Kerfoot *et al.* 1994). Copper fluxes from McNearney Lake (Cook *et al.* 1990), an isolated kettlehole seepage lake 5.4 km south of Whitefish Bay, were contrasted with a station in the center of Whitefish Bay (Ile Parisienne Basin), located immediately north of McNearney Lake in Lake Superior. Total deposition of Cu between 1880 and 1973 in McNearney Lake was low (inventory of 32 µg/cm<sup>2</sup>; mean flux 0.34 µg/cm<sup>2</sup>/yr), increasing from 0.1 to 0.2 µg/cm<sup>2</sup>/yr to peak at 0.7 µg/cm<sup>2</sup>/yr around 1960. The maximum value agreed with direct measurements of atmospheric deposition from the 1970s (0.7 µg/cm<sup>2</sup>/yr; Kunz in Nriagu 1979). Total copper deposition at the Whitefish Bay site over the same interval (1880 to 1973) was high, 495 µg/cm<sup>2</sup>, with a background

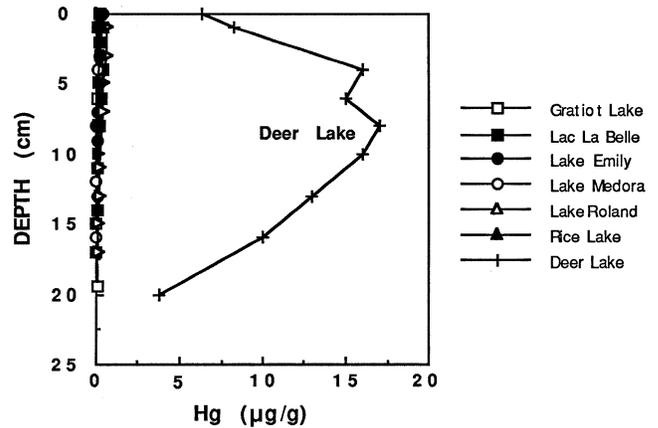
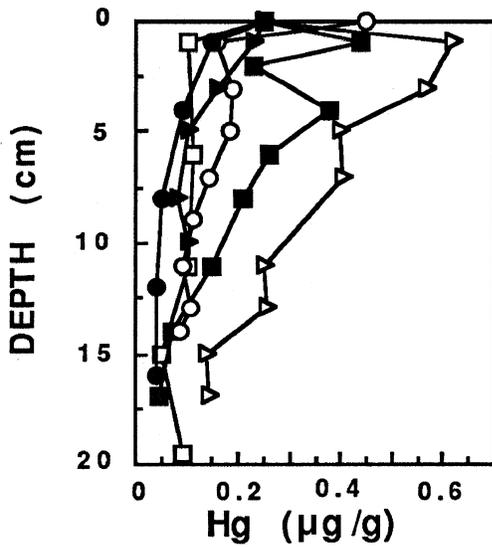
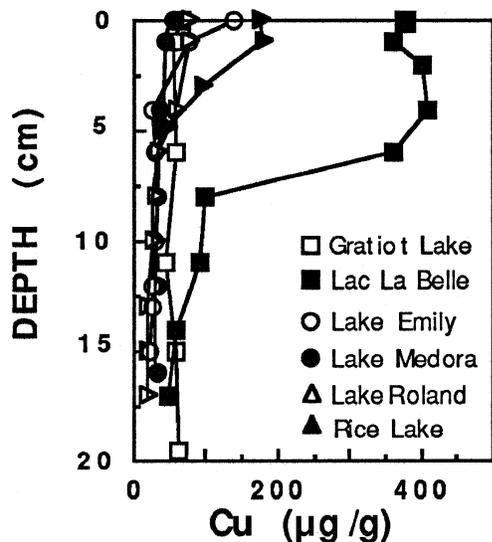
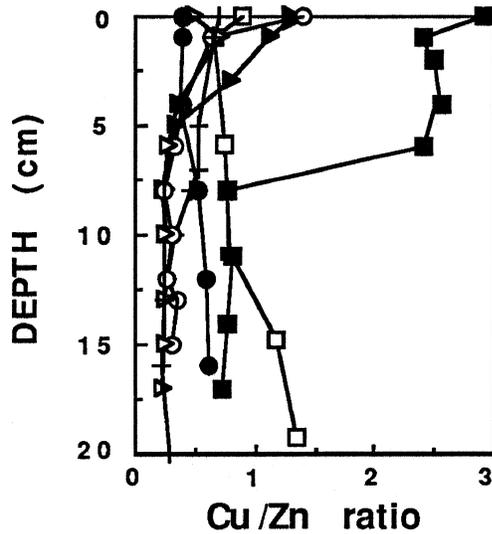


FIG. 10. Mercury concentration profiles from the Michigamme Project lakes, illustrating the extreme values for Deer Lake.



estimated input of 186  $\mu\text{g}/\text{cm}^2$  (37.6% total), giving an anthropogenic inventory of 495 – 186 = 309  $\mu\text{g}/\text{cm}^2$  (62.4% total). If the McNearney Lake total correctly estimated regional atmospheric input, atmospheric deposition accounted for 6.5% of the total (i.e., 32/495). However, The Whitefish Bay estimate is a single nearshore estimate and neither it nor the revised Kemp estimate incorporated corrections for sediment focusing.

Recently, Kolak *et al.* (1998) estimated regional atmospheric flux at 0.13 to 0.19  $\mu\text{g}/\text{cm}^2/\text{yr}$  from three OMEE (Ontario Ministry of Environment and Energy) monitoring sites. Estimated copper fluxes were low at five, largely deep-water core sites, ranging between 0.59 and 1.48  $\mu\text{g}/\text{cm}^2/\text{yr}$ . The mean inventory was estimated to be 52  $\mu\text{g}/\text{cm}^2$ , corrected for focusing. The Kolak *et al.* study estimated that atmospheric contributions ranged between 21 to 38% of total input. Yet this high value is largely because of low total copper inventories at chosen core sites (predominantly mid-lake and western basin), and more correctly reflects deep-water, rather than total, Lake Superior deposition patterns.

Published mass deposition rates at the coring sites in this study (Table 3) allow additional esti-

FIG. 9. Profiles for Hg concentration, Cu/Zn ratio, and Cu concentration in sediment cores from Michigamme Project lakes. Symbols in lower right identify samples from specific lakes.

mates of lake-wide fluxes. Three nearshore stations directly influenced by mining discharges revealed very high fluxes (I7 19.87  $\mu\text{g}/\text{cm}^2/\text{yr}$ ; KB 9.90  $\mu\text{g}/\text{cm}^2/\text{yr}$ ; T46A 7.17  $\mu\text{g}/\text{cm}^2/\text{yr}$ ). Including these values gave a mean Cu loading of  $5.02 \pm 2.50$   $\mu\text{g}/\text{cm}^2/\text{yr}$  to Lake Superior, whereas dropping the three high sites reduced the estimated loading to  $3.35 \pm 1.17$   $\mu\text{g}/\text{cm}^2/\text{yr}$ . Using the mean McNearney value for atmospheric deposition (0.34  $\mu\text{g}/\text{cm}^2/\text{yr}$ ), an estimated atmospheric contribution is obtained of 6.8% for the total or 10.1% if the high coastal sites are dropped. Use of the OMEE atmospheric estimates results in much lower values (3 to 6%). Thus the values reported here are in good agreement with the corrected Kemp estimates, but considerably less than that estimated by Kolak *et al.* (1997). Atmospheric loading of Cu to Lake Superior appears to be less than 10% of total copper loading.

### Mining Signature

Previous work on Cu suggests strong offshore-nearshore gradients, where solution dynamics dominate offshore regions, whereas particle dynamics dominate nearshore regions. In the oligotrophic offshore waters of Lake Superior, most work on trace element cycling has examined accumulation and early diagenesis only in the solid-phase of near-surface sediments. Enrichments of several trace metals (Cu, Zn, Pb, rare earth elements) are recognized and attributed to near-surface oxic precipitation of Fe and Mn, metals that are mobilized under reducing conditions at greater sediment depths (McKee *et al.* 1989a, McKee *et al.* 1989b, Olivarez *et al.* 1989, Richardson and Nealson 1989). If copper is also mobilized, then buried maxima could reflect redox gradients, rather than historic events. If overall losses are minimal, inventories would still be accurate. At some sites, diagenetic enrichments appear to be overwhelmed by high concentrations of trace metals, presumably anthropogenic, in fine near-bottom suspended particles and unconsolidated surface sediment (McKee *et al.*, 1989a). The latter observations are fully compatible with long-range transport of slime clay particles. Diagenetic release of Hg from central lake sediments also has been shown (Matty and Long 1995), yet the sources (atmospheric, terrigenous) are not clearly identified.

Sediment cores taken in nearshore environments document early deposition and high inventories of Cu and Hg at several sites around the coastal region of Lake Superior. Copper concentrations and cop-

per to zinc ratios are particularly high in cores across the southern portion of the eastern basin, at core depths that correspond to the initiation of turn-of-the-century mining activities. The high correlation between the Cu/Zn ratio and the absolute copper concentration suggests that mining had a widespread influence. The nearly simultaneous increase of mercury with copper, high silver:mercury correlations, examples of buried mercury maxima, and higher mercury inventories all suggest shoreline sources of mercury (Harting *et al.* 1996).

It is likely that the mercury contamination associated with mining activity in the Keweenaw came from two primary sources: 1) present in copper ore lodes as a natural amalgam, dispersed in tailing discharges and released during smelting, and 2) discarded as a by-product of early amalgamation extraction or assay techniques. The natural amalgam hypothesis explains many patterns. Direct assays of copper ores reveal moderate to high Hg concentrations. Silver-mercury correlations in core samples also suggest natural mineral associations. Silver and gold ores often contain mercury in small quantities as a natural amalgam. Silver is characteristic of copper lodes around Lake Superior, producing the highly valued "Lake Copper" alloy (Cronshaw 1921). On the Keweenaw Peninsula, native copper mines yielded about 1 part of silver per 1,000 parts of copper. For example, in 1918 electrolytical refining yielded 56,127,000 lb of copper and 509,467 oz of silver. By 1977, Michigan copper mines recorded production of over 5 billion kilograms of copper (Weege and Pollack 1971) and over half a million kilograms of silver (16,469,544 troy ounces). However, actual silver production was probably twice the recorded total, because of miners and mine managers pocketing nuggets (Olson 1986). Small amounts of silver were found in virtually all the lodes mined on the peninsula, but some copper mines were rich enough to be considered initially as silver mines (Isle Royale, Huron, Portland, Sheldon, and Columbian mines near Portage Lake). A more southern cluster of mines, associated with the Nonesuch Shale, was known as the Silver City district (Carp Lake Mine 1858, Cuyahaga Mine 1860, Lafayette Mine 1860, Porcupine Mine 1860, Cleveland Mine, Union Mine 1865, Scranton Mine 1973, Superior Mine 1873, Collins and Delevan Mines, Nonesuch Mine 1867, Halliwell Mine 1896, White Pine Mines 1914, 1915).

Amalgamation extraction techniques were rare in the northern native copper lodes, where separation relied on crushing the rock under steam-driven

stamps, followed by gravity separation in jigs and "slime" separation on Wilfley Tables (Benedict 1955). However, in the silver district of Michigan, stamp mills often featured amalgamation techniques for extraction of silver (Ontonagon Silver Works; Swineford 1876; Jamison 1950). Determining amalgamation activity and mercury use from company records is difficult, although yearly expense sheets list "amalgamators" under labor costs and document the cost of mercury not recovered during processing ("loss of mercury, 3/4 lb. per ton ore" Swineford 1876). The loss of mercury in the mills of western United States generally varied from 0.3 to 3.0 kg/tonne of silver ore treated (Nriagu 1994). The increasing rates of atmospheric mercury deposition reported in midcontinental North America (Swain *et al.* 1992) may contain accumulative effects of Hg vaporization from mine tailing piles and amalgamation heaps (Nriagu 1994).

Smelting apparently broadcast copper and mercury-rich plumes across downwind watersheds. Whereas much of the mercury associated with silver in sediments may be mineral-bound, a genuine concern is vaporization from tailing piles or that high methylation rates of mercury may occur in wetlands located downwind from smelters or along lake estuarine habitats where humic-stained waters pass through stamp sand strata. High methylation rates are due to a combination of a favorable environment for methylating bacteria (rich source of organic material) as well as greatly fluctuating water tables, accentuated along the southern shoreline of Lake Superior by "lake effect" precipitation.

Long distance dispersal of tailing particles ("slime clay" portion) by the Keweenaw Current and subsequent dissolution in the Caribou basin is a concern. Long distance dispersal of mining tailings is not without precedent in Lake Superior. Between 1955 and 1980, approximately 500 million tons of taconite tailings were discharged near Silver Bay, Minnesota, by Reserve Mining Company. This is a mass equivalent to the entire discharge from a century of copper mining in the Keweenaw Peninsula of Michigan. Iron-rich sediments moved into the Duluth basin, considerably beyond the confines of the permitted 9-square mile dumping site. Small asbestiform particles from the discharge spread widely over three western basins of Lake Superior (Duluth, Chefswet, and Thunder Bay basins), most noticeably impacting core site I7. These particles are now located several hundred kilometers from the original discharge site (Cook *et al.* 1974, IJC

1977, Cook *et al.* 1985). More recently, Cook (personal communication) uncovered evidence that the asbestiform particles have now moved throughout the entire lake, presumably due to long-term processes of sediment resuspension and focusing. Thus the copper and iron mining studies of Lake Superior sediments underscore one fundamental principle: deposition of any fine grain materials into the high-energy nearshore environment of Lake Superior, especially into the littoral scour zone, will result in eventual movement of this material tens to hundreds of kilometers from the original site of deposition.

### CONCLUSION

With regard to metal cycling, rather than viewing the Lake Superior watershed as a pristine environment under assault solely from long distance atmospheric discharges, the lake is more appropriately viewed as an ecosystem that was disturbed earlier by turn-of-the-century mining in a patchwork manner along the shoreline. Portions of the lake are in a recovery phase, whereas other areas are still impacted by slow resuspension-deposition dynamics and by continuing mining activities. Previously contaminated nearshore sediments are undergoing a combination of deep burial and gradual circulation into deep, net-deposition basins. Transport is influenced by several physical and biogeochemical processes that redistribute metals and that perpetuate elevated fluxes, although coastal and deep-water dynamics will probably differ in process details.

High copper-mercury concentrations can be traced back to shoreline stamp mills and smelters. Elevated mercury occurs in nearshore stamp sand sediments, occurring as a natural amalgam with silver and copper. Several smelting operations also discharged copper and mercury-enriched plumes, blanketing watersheds downwind. Elevated trace metal profiles are present in sediments of inland lakes, are derived from both milling and smelting practices, and suggest elevated regional cycling of copper and mercury. The net effect of historic smelter and mining activities interacting with natural humic substances from juxtaposed wetlands is a concern. Whereas organic complexation of copper will reduce toxicity and accelerate removal to sediments, a beneficial consequence, corresponding methylation of mercury may increase toxicity and decrease deep burial in sediment of this element.

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