Local, Regional, and Global Implications of Elemental Mercury in Metal (Copper, Silver, Gold, and Zinc) Ores: Insights from Lake Superior Sediments

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ABSTRACT. *Anthropogenic inventories for copper (229 ± 89 ug/cm^2, N = 30), and mercury (470 ± 307 ng/cm^2, N = 25) in Lake Superior sediments are much greater than inventories in remote lakes (Cu 50 ± 31 ug/cm^2, Hg 64 ± 34 ng/cm^2, N = 16) that receive inputs largely from long-distance atmospheric sources. Whereas the absolute concentration of mercury in Lake Superior sediments is not high (80–110 ng/g), enrichment ratios along coastal margins indicate industrial sources. An example of previously unreported mining-related inputs comes from native copper mining on the Keweenaw Peninsula. Around the peninsula, sediment inventories for mercury, silver, and copper are highly correlated and can be traced back to shoreline tailing piles, smelters, and parent ores. Elemental mercury occurs as a natural amalgam or solid solution substitution in native metal (copper, silver, gold) deposits and associated gangue minerals (e.g., sphalerite, ZnS) at µg/g or higher concentrations. Native copper stamp mills discharged more than 364 million metric tons of "stamp sand" tailings, whereas copper smelters refined five million metric tons of copper, liberating together at least 42 metric tons of mercury. Release of trace mercury from Lake Superior mining deserves regional attention as preliminary estimates resemble EPA Region #9 patterns and could help explain the 4–7 fold sediment inventory discrepancies. We show that the Keweenaw situation is not unique geographically, as mineral-bound trace mercury is commonplace in U.S. and Canadian Greenstone Belts and of worldwide occurrence in precious (gold, silver) and massive base metal (copper, zinc) ore deposits.*

INDEX WORDS: *Sediments, Lake Superior, mining, trace mercury, base metal ores, copper smelting, gold, silver, copper, mercurian sphalerite, mercury release, mercury inventories.*

INTRODUCTION

The Lake Superior watershed is under consideration as a Zero-discharge Region for mercury by the Lake Superior Binational Program (LSBP 2002). Because progress toward such a designation requires information about past and present mercury sources and cycling, here we emphasize that 1) anthropogenic inputs from mining and industrial centers are superimposed upon long-distance deposition patterns, often locally overriding these signals, and 2) regional rock sources of mercury have contributed to mercury sediment fluxes (erosional and anthropogenic inputs). These ancillary sources help to explain why Lake Superior anthropogenic metal

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inventories are greater than expected from long-distance atmospheric transport. Thus our viewpoint differs from the 1998 International Joint Commission (IJC 1998) opinion that mercury loading in Lake Superior sediments is largely attributable to long-distance atmospheric sources, and is more aligned with recent UNEP (2002), Environment Canada (2000), and Region 9, U.S. EPA (2003) perspectives that mining contributions are substantial in North America and worldwide.

Within the Lake Superior watershed, there are recognized historical anthropogenic sources for copper, such as tailings piles (Benedict 1955, Kerfoot *et al.* 1994, Kerfoot and Nriagu 1999) and for mercury, such as coal-burning power plants, slimicides from pulp and paper mills, chloralkali plants, municipal incinerators, and mining regions (IJC 1977, Bissett and McBeath 1988, Glass *et al.* 1990, Harting *et al.* 1996, Kerfoot *et al.* 1999, Rossmann 1999). However, the source and fate of mercury associated with exploited metals (silver, copper, gold) has not been examined in detail, and an intimate geological association may have important implications for studies of regional and global mercury cycling.

Here we underscore the magnitude of historic copper inputs into Lake Superior and illustrate how mercury and copper sediment profiles around the Keweenaw Peninsula can be traced back to a common source. Two early investigators of Lake Superior sediments, Nussman (1965) and Kemp *et al.* (1978), suspected that copper enrichments in Lake Superior sediments originated from several intensively mined regions: the Keweenaw Peninsula of Michigan and the Thunder Bay, Marathon, Wawa, and Sault Ste. Marie regions of Ontario, Canada. On Michigan's Keweenaw Peninsula, native copper and silver were recovered from parent rock by stamping (i.e., crushing rock using steam-driven stamps). Poor-rock piles (rock removed from mines, but deemed too poor in Cu for transport to stamp mills) lie scattered about the landscape, and at least 0.36 billion metric tons of copper-rich stamp sands were sluiced into streams, interior waterways, and along Lake Superior shorelines, with additional amounts contributed from numerous early small operations (Kerfoot *et al.* 1994, Kerfoot and Robbins 1999, Jeong *et al.* 1999). Smelters along the Keweenaw Waterway refined five million metric tons of native copper from 1889 to 1968, working ore from the Portage Lake Lava Series and the Calumet Conglomerate. Between 1952 and 1995, an additional 1.8 million metric tons of copper and silver were smelted from the chalcocite-bearing Nonesuch Shale at White Pine, Michigan.

Elevated copper concentrations in sediments near the Keweenaw Peninsula can be traced back to tailings piles (Kerfoot *et al.* 1994, Kerfoot and Robbins 1999, Kolak *et al.* 1999). Neutron activation procedures provided a 32-element end member analysis which matched sediment composition with shoreline sources (Kerfoot and Robbins 1999). Unfortunately the neutron activation studies did not include mercury.

In addition to long-distance regional atmospheric deposition, there are two potential local mining sources for atmospheric mercury, one imported and one geological. One potential pathway is via re-emission of mercury imported for amalgam extraction of gold or silver, whereas the other pathway is through flue emission from smelters and ore refining operations. An unappreciated potential source of mercury from historic mining comes if the element occurs naturally in solid solution within ores. Since the 1950s, detection of "mercury halos" has been standard practice for locating precious metals (gold, silver) and massive sulfide metal deposits (Cu, Zn, Pb ores: Saukov 1946; Ozerova 1985, 1986). If mercury also occurs as a natural amalgam in gold, silver, or copper, or as a solid solution substitution in accompanying gangue minerals, it would be released as a result of discharging tailings, processing concentrates, or smelting ores.

Mercury, silver, gold, copper, lead, and zinc are all similar with respect to their formation and geological occurrence. In the free state ($Hg°$), mercury can form naturally-occurring amalgams with gold, silver, or copper-silver mixtures. Natural alloys with silver are recognized, e.g., kongspergite [α-(Ag,Hg)] and moschellandsbergite [γ-(Ag,Hg)], whereas alloys with gold are more scarce (Boyle 1987). Mercury can exist in combined mineral form (e.g., cinnabar HgS, coloradoite $HgTe$, tiemannite $HgSe$), although cinnabar is not commonly recognized in the Lake Superior region (but see Discussion). However, an amalgam form "arquerite," or mercurian silver ($Ag_{12}Hg$), was documented at the Silver Islet mine near Ontario's Sibley Peninsula, along Thunder Bay (Wilson 1986). Because silver is characteristic of Lake Superior native copper lodes, producing the historically valued "Lake Copper" alloy (Cronshaw 1921), we examined the possibility that trace mercury occurs in solid solution as a natural amalgam or in associated minerals. In the process, we discovered that the ubiquitous mineral sphalerite, an isotype (similar geometry, similar composition) of several Hg minerals [e.g., metacinnabarite

(HgFeZn)S, coloradoite HgTe, tiemannite HgSe], may also be very important, as Hg substitutes in solid solution within its chemical lattice.

If naturally-occurring mineral-bound mercury was emitted during routine ore processing and contributed substantial amounts to nearby sediments and wetlands, this historical discharge could be generating MeHg to the regional watershed and atmosphere (Hurley *et al.* 2001). Here we show how local mining is historically intertwined with atmospheric Hg contributions by looking at stamp sand and smelting inputs. In a broader context, we emphasize that the implications of trace mercury from ore deposits extend across the continent to metal processing activities in general and to global mercury cycling.

METHODS AND MATERIALS

Sediment Cores

Thirty-two cores were taken from the R/V *Limnos* in 1983 as part of a National Water Research Institute program (study leader Rick Bourbonniere) and archived at the National Oceanic & Atmospheric Administration's Great Lakes Environmental Research Laboratory (NOAA/GLERL, Ann Arbor, MI). Sampling sites were distributed over several offshore and nearshore 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
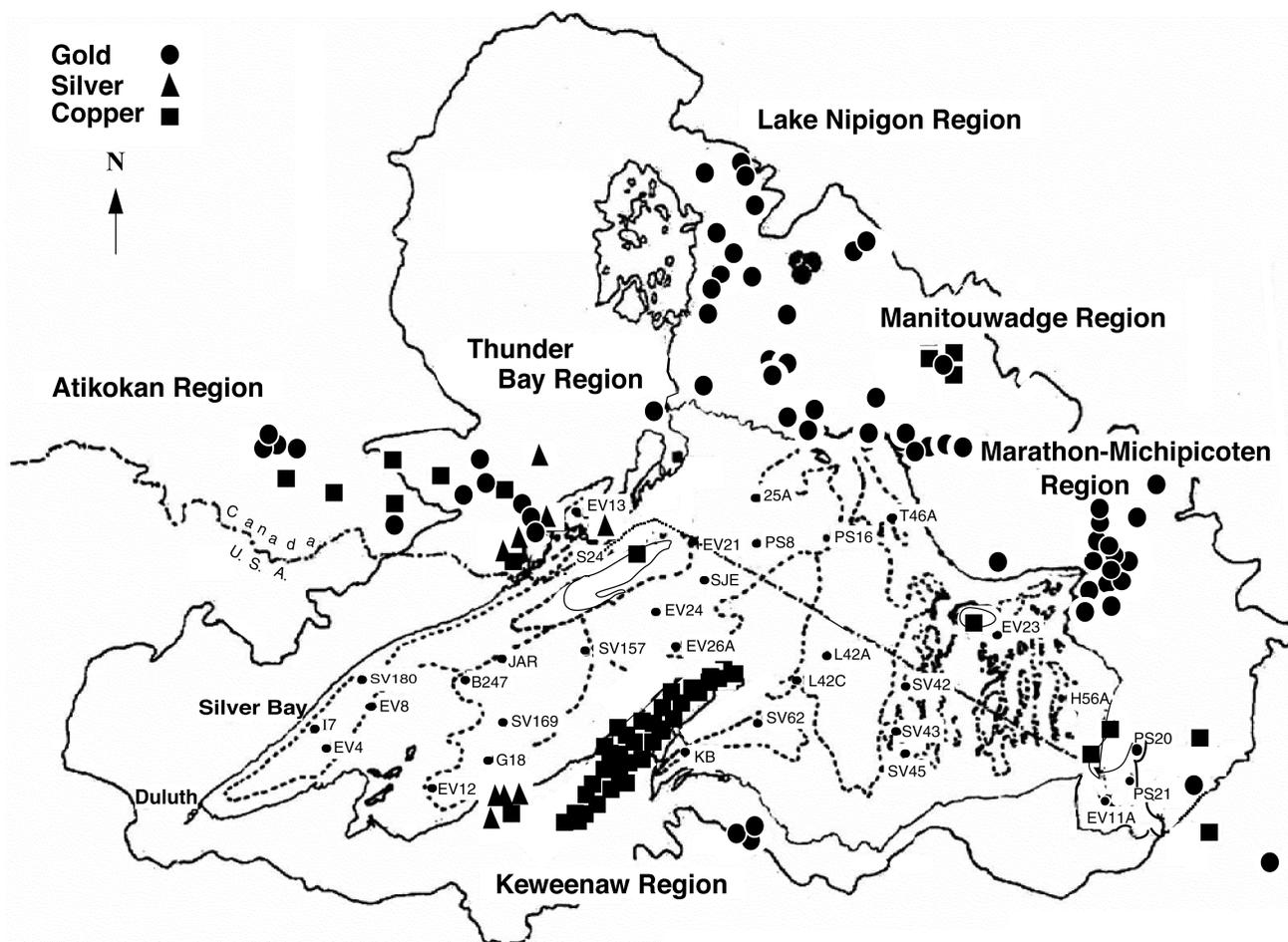

FIG. 1. *Precious and base metal mining regions of the Lake Superior watershed (copper, silver, and gold sites) with locations of the 1983 Lake Superior coring sites. Drainage basin boundaries are indicated by a solid line and the international boundary (U.S., Canada) by an uneven broken line. Lake Superior sedimentation basins (even broken lines) are shown relative to the location of inventory cores.*

Superior eastern troughs (SV42, SV43, SV45, H56A), Wawa trough (EV23), Batchwana Bay (PS20), Goulais Bay (PS21), and Whitefish Bay (EV11A). Cores were collected using a 7.6 cm diameter gravity corer that was lowered carefully into the sediment, minimizing loss of surface layers and reducing compaction artifacts. All cores were sectioned immediately upon retrieval. The majority 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.

An additional 84 cores were taken along the southern shoreline of Lake Superior and from inland lakes near the Keweenaw Peninsula between 1996-2000 (Figs. 2a,b). Cores from Chequamenon Bay (2), L'Anse Bay portion of Keweenaw Bay (3), Keweenaw Waterway (19), and small inland lakes (16) were obtained with a KB Wildco gravity corer (5.1 cm diameter plastic liner). Liners were washed thoroughly prior to coring and leached in 10% nitric acid. The coring device was lowered slowly, using a Lowrance model X-16 sonar unit to help position the corer 1-2 m above sediments prior to release. Extruded sediment was sliced into 1–2 cm sections, weighed, and subsampled for dry weight determinations and metal analysis.

Within the 1996–2000 total, 44 cores were taken around the Keweenaw Peninsula by Multicorer and box corer from the R/V *Blue Heron* and R/V *Laurentian* as part of the KITES NSF/NOAA CoOP Project. Twenty-two cores (22) from the *Laurentian* box corer are utilized here. The *Laurentian*'s large capacity box corer (50 cm × 50 cm area × 60 cm deep) allowed us to insert multiple KB core tube liners into the mud sample, providing undisturbed, replicate sampling of sediments. The box cores were sliced at 1cm intervals down to 40 cm. Two additional cores were obtained by hand lowering core tubes into wetland sites (LM, SEW) adjacent to the Keweenaw Waterway.

In order to determine the correlation between Cu and Hg concentrations in a grid-sampled, homogeneous set of modern-day Lake Superior sediment samples, we obtained 69 Ponar samples from the southern region of Keweenaw Bay during August of 2002. The Ponar samples were taken from the R/V *Navicula* over a range of water depths (2.7–99.4 m; Fig. 2b).

Sediment subsamples for metals analysis were air dried and homogenized by grinding to a fine powder. 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. The archived 1983 samples were digested using a CEM microwave digester. Filtrate samples (0.45 μm Gelman Supor-450) were analyzed at the Environmental Protection Agency (EPA) Grosse Ile, MI, lab for total mercury using the cold vapor technique with a Perkin-Elmer AA and a Perkin-Elmer MHS-20 mercury/hydride system. Copper and silver in the 1983 samples were analyzed at Michigan Technological University (MTU) using flame AA (Perkin-Elmer Model 5000). Based on the standard deviation of blanks, the detection limit for mercury was 5 ng/g at the typical weight of sample extracted. Approximately 16% of all analyses were blanks, standard reference materials, and replicate extracts of samples. Standard Reference Material (SRM 2704a, Buffalo River Sediment, National Bureau of Standards, NIST 1990) checked metal extraction efficiency. Copper recovery (N = 20) was 93.2 ± (1 SD)7.1%, and Hg was 96.7 ± 9.0%. The certified concentration for mercury in SRM 2704 was 1.47 μg/g. Replicate Cu samples (N = 20) from cores were 90.4 ± 4.8% similar.

For the Keweenaw Peninsula, Keweenaw Waterway, and small inland lake core samples, digestion was performed in a Milestone Ethos 900 microwave digester at MTU. All samples were analyzed for copper and silver by flame AA using the Perkin-Elmer Model 5000 mentioned earlier. Total mercury was analyzed by the cold vapor technique with a Perkin-Elmer Model 5000 and a Perkin-Elmer MHS-10 mercury/hydride system. For every set of 10 samples, a minimum of two sets of standards, two procedural blanks, and one duplicate sample were run. To ensure quality control and quality assurance (QC/QA), selected sample extracts (5% total) were split and analyzed independently at the Grosse Ile lab. There was 90.4% (range 73.0–98.6%) agreement between the results of the Grosse Ile Lab and MTU analyses. At MTU, to measure extraction efficiency, we routinely compared our results to Standard Reference Material (Natural Matrix Certified Reference Material; "Metals of Soil/Sediment #4," from Ultra Scientific). The concentration of copper in the standard was 98.6 μg/g, whereas Hg was 720 ng/g. Copper recovery (N = 15) was 90.0 ± 11.6% and Hg was 96.7 ± 9.0%. Replicate core samples (N = 16) gave the following agreement values: Cu 90.4 ± 5.8%, Hg 91.1 ± 4.5%.

The 1983 cores were analyzed for copper, silver, mercury, and [137]Cs. [137]Cs inventories (Fig. 3) for NOAA and Portage Lake cores were determined at the GLERL laboratory, following procedures outlined in Robbins and Edgington (1975), Kerfoot *et*
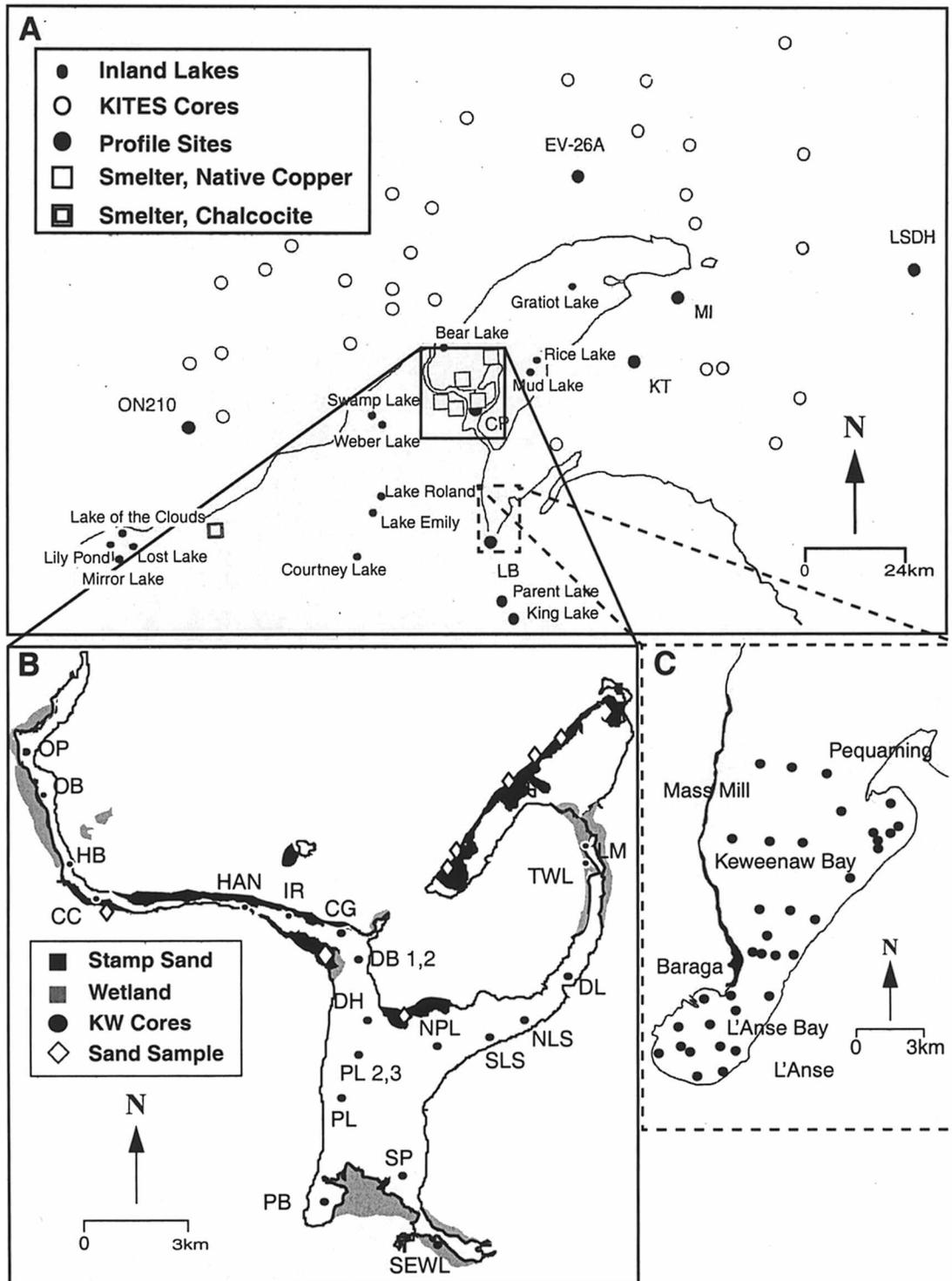
FIG. 2.   Coring sites near or on the Keweenaw Peninsula: a) KITES coring sites around the Keweenaw Peninsula and small lake locations. Large solid dots with letters indicate sites shown in Figure 7. Smelter sites are designated by squares (names in text). Ponar sampling area in Keweenaw Bay marked by a dashed rectangle. b) An enlargement of the Keweenaw Waterway showing coring and stamp sand sampling locations and c) of L'Anse Bay showing ponar sampling locations. Stamp sand tailing piles are indicated in black, whereas wetlands are stippled.

A

B
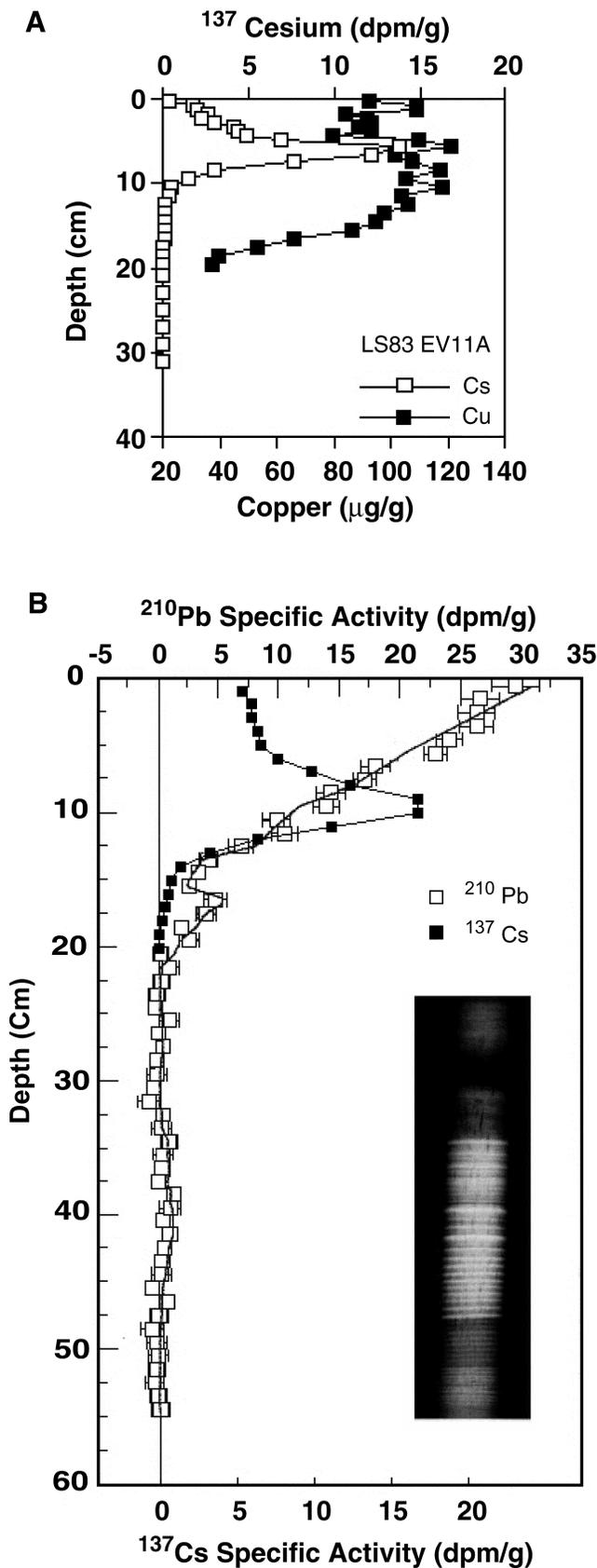
al. (1994), and Kerfoot and Robbins (1999). Samples were counted in standardized geometry using a high-resolution gamma detector coupled to a multichannel analyzer. The efficiency of the detector was determined with sediments doped with precisely known (<1%) amounts of an National Bureau of Standards-traceable mixed-radionuclide standard solution (Amersham QCY46.1) counted in the same standard geometry. ^{137}Cs was determined, from its 661.6 KeV gamma emission, with a precision generally better than 5% for counting times of ~1 day.

We also measured the activity of ^{210}Pb and ^{226}Ra in the upper 20 cm of a central core from Portage Lake both to confirm ^{137}Cs dates and to bridge the intervals dated by ^{137}Cs and varve dating (Kerfoot and Robbins 1999). Under conditions of highly variable accumulation rates, measurements of ^{210}Pb and ^{226}Ra are required. The efficiency of detection was checked using samples of the same sediment spiked with a well-determined amount of NIST standard solution of ^{226}Ra. Uncertainties in determination of ^{226}Ra were 5% or less. The efficiency for detection of ^{210}Pb was checked from the same ^{226}Ra spike which had a known amount of ^{210}Pb activity arising from in-growth. The amount of ^{210}Pb in the standard solution was determined from an NIST-calibrated ^{210}Pb solution provided by the U.S. EPA. The limit of detection of ^{210}Pb activity was about 0.9 dpm/g. Near the top of the core, uncertainties were around 3%, but increased to 20% in the region of background below about 20 cm depth (Kerfoot and Robbins 1999). X-rays of cores from the Keweenaw Waterway revealed a rich sequence of varve-like Cu-rich clay bands that could be correlated closely with the reconstructed mill discharge histories down to 1860 (Fig. 3, see cross-correlation in Kerfoot *et al.* 1994, Kerfoot and Robbins 1999).

Stamp Sand, Poor Rock, and Native Ore Samples

We collected tailings samples from ten "stamp sand" piles and five poor rock piles. Metal ore sam-

FIG. 3. *Radioisotope profiles from Lake Superior and the Keweenaw Waterway: a)* ^{137}Cs *profile from a finely sliced 1983 core (EV11A), and b)* ^{137}Cs *and* ^{210}Pb *profiles from Portage Lake with an insert of X-ray bands in Portage Lake cores.*

ples were obtained from 29 different mine sites. Lists of individual sample locations, voucher numbers, and metal concentrations are on file at the Seaman Mineral Museum Collection (Michigan Technological University, MTU). Cleaned metal samples were digested in reagent-grade nitric acid and analyzed for total mercury, silver, and copper (Methods, Sediment Cores).

Small, Isolated Inland Lakes

To estimate regional atmospheric fluxes of copper and mercury, we took sediment cores from 15 small, isolated lakes using the Wildco KB gravity corer. The lakes were distributed over an area of 3,275 square kilometers (Fig. 2a) near or on the Keweenaw Peninsula. None of the lakes had any previous history of industrial activity other than regional logging.

Sediment cores were analyzed as before (Methods, Sediment Cores). Ragweed (*Ambrosia*) is an exotic opportunist species that appears at the time of land clearance. In the western Upper Peninsula, clearance took place around 1900 in non-mining areas and around 1870 near active mining operations (Brubaker 1975, Davis 1978). We utilized the date of the ragweed horizon to determine background levels of metals, to estimate sedimentation rates, and to calculate mercury and copper inventories and fluxes (see Harting 1999, Kerfoot *et al.* 2002 for details).

Inventory Calculations

The chemical inventory of a contaminant is defined as the concentration of the contaminant of interest above background per unit area, integrated over the entire depth of the sediment core (Eisenreich *et al.* 1989). In practice we determined inventories (S_a) for anthropogenic copper, silver and mercury by summing products of excess metal concentrations ($C_i – C_b$) and dry weights of solids ($\rho_i d_i$) over those (n) core sections with significant excess concentration. The term C_i is the concentration (μ/g or ng/g) in the ith core section and C_b is the background concentration, ρ_i is the bulk dry density of solids (g cm^{-3}) and d_i is the thickness (cm) of the section. Mathematically,

$$S_a = \sum_{i=1}^{n}(C_i - C_b)\rho_i d_i \qquad (1)$$

where the units of S_a are μ/cm^2 or ng/cm^2. We calculated excess (or anthropogenic) metal accumulation rates for ith core sections as

$$Fa_i = (C_i – C_b)R_s \qquad (2)$$

where R_s = is a radiometrically determined net mass accumulation rate (g cm^{-2} yr^{-1}). Units of Fa_i are either μg cm^{-2} yr^{-1} or ng cm^{-2} yr^{-1}. In the 1983 series, deposition rates for 16 core sites were derived from literature values based on close-interval sectioned cores taken at the same sites and checked using ^{137}Cs profile peaks (Fig. 3).

Sediment focusing, however, can redistribute sediment in a non-uniform manner across the lake bottom, requiring corrections. In the 1983 2 cm-sectioned cores, we could use the ^{137}Cs inventories to correct for sediment focusing across the irregular bottom topography of Lake Superior, using an expected mean value of 24.0 dpm/cm^2 derived from decay-corrected atmospheric deposition (Kerfoot *et al.* 2002). That is,

$$F = \text{focusing factor} =$$
$$\text{Observed/Expected } ^{137}\text{Cs inventory} \qquad (3)$$

Inventories or fluxes from the 1983 cores were corrected by the focusing factor, i.e., S_a/F or R_i/F. The correction assumes initial uniform atmospheric deposition across the lake surface, but may be sensitive to particle scavenging along coastal margins.

Storage Estimates

Mercury inputs from stamp mills and smelters were calculated by multiplying the mean concentration of mercury by the total mass discharged or processed. Mean mercury concentrations came from tabled values listed here and in Kerfoot *et al.* (2002), whereas stamp mill discharge totals were taken from Kerfoot *et al.* (1994). In local reverberatory smelter furnaces, coal heating furnished an indirect flame over the prepared ore material (Lankton 1997a, b). Smelting was assumed to volatilize 100% of mercury contained in copper up four low stacks situated at the corners of the smelter building. This estimate is probably low-biased because it does not include mercury in gangue minerals that accompanied the copper nor coal burned during furnace operations. Mercury storage in Keweenaw Waterway sediments was calculated based on sediment core inventories and the areal extent of lake deposits (combination of U.S. Geological Survey Topographic sheets and sonar surveys; see Harting 1999 for details on calculations).

TABLE 1. Metal fluxes and anthropogenic inventories for small lake, Lake Superior, and Keweenaw Waterway sites (N = sample size, mean with 95% confidence intervals). Lake Superior values given as observed ("uncorrected") and focusing-corrected ("corrected").

Surface Fluxes

Copper (μg/cm²/yr)	N	Range	Mean ± 95 C. L.	
Small Lake	16	0.2–1.9	0.4 ± 0.2	
Lake Superior	16	1. –7.7	3.0 ± 1.0	(corrected)
Lake Superior	16	1.1–19.9	5.0 ± 2.5	(uncorrected)
Keweenaw Waterway	18	3.0–57.0	25.5 ± 8.2	
Mercury (ng/cm²/yr)				
Small Lake	16	0.5–2.4	1.1 ± 0.4	
Lake Superior	19	0.8–10.0	3.9 ± 1.4	(corrected)
Lake Superior	19	1.0–36.0	7.3 ± 4.8	(uncorrected)
Keweenaw Waterway	14	2.1–41.1	10.9 ± 6.9	

Anthropogenic Inventories

Copper (μg/cm²)				
Small Lake	16	1–180	50 ± 31	
Lake Superior	30	45–472	161 ± 33	(corrected)
Lake Superior	30	47–1,130	229 ± 89	(uncorrected)
KITES	22	10–2,968	497 ± 407	
Keweenaw Waterway	21	1,081–20,163	8,571 ± 2,264	
Mercury (ng/cm²)				
Small Lake	16	67–298	64 ± 34	
Lake Superior	25	6 –1,858	293 ± 165	(corrected)
Lake Superior	25	41–4,460	470 ± 307	(uncorrected)
KITES	22	19–487	206 ± 63	
Keweenaw Waterway	23	187–7,758	2,696 ± 854	

RESULTS

Anthropogenic Fluxes and Inventories in Remote Lakes

In the small lake survey (Fig. 2a, Table 1), our mean estimate of atmospheric copper flux was 0.39 ± 0.24 μg/cm²/yr. This value compared well with previous small lake estimates (0.31 μg/cm²/yr, Upper Peninsula of Michigan, Sweet *et al.* 1998; 0.32 μg/cm²/yr, McNearny Lake, MI, Cook *et al.* 1990, Kerfoot *et al.* 1994), but was much less (1/10th) than the 1983 focusing-corrected Lake Superior mean surface flux (3.0 ± 1.0 μg/cm²/yr). Similarly, surface mean mercury flux to small lakes was 1.1 ± 0.4 ng/cm²/yr, also close to previous regional estimates (1.3 ng/cm²/yr, Minnesota lakes, Swain *et al.* 1992; 1.0 ± 0.3 ng/cm²/yr, mid-continent lakes, Fitzgerald *et al.* 1991), but again less (1/3rd) than the focusing-corrected 1983 Lake Superior surface mean mercury flux (3.9 ± 1.4 ng/cm²/yr).

Inventory comparisons, which integrate over the past 1 1/2 centuries and separate anthropogenic from background inputs, also revealed that remote small lakes had much lower mean anthropogenic inventories for copper (50 ± 31μg/cm²) than focusing-corrected Lake Superior sites (161 ± 33 μg/cm²). Smaller inputs were also recorded for mean anthropogenic mercury, 64 ± 34 ng/cm² for small lakes compared to 293 ± 165 ng/cm² for focusing-corrected Lake Superior sites. If fluxes and inventories in small lakes are indicative of atmospheric deposition, then there is substantially more copper and mercury in Lake Superior sediments than expected from atmospheric deposition in small, remote lakes.

In Lake Superior, anthropogenic Cu inventories uncorrected for focusing varied from 47 to 1,130 μg/cm² (229 ± 89 μg/cm²), about 4.6× the value from small, remote lakes. Anthropogenic Hg inventories uncorrected for focusing varied from 41 to 4,460 ng/cm² (470 ± 307 ng/cm²), around 5–7× the small lake value (Table 1).

Magnitude of the Keweenaw Copper Mining Discharge

Total copper inventories for Lake Superior cores were high relative to the other Great Lakes (613 ±

120 µg/cm^2 for 20 cm depth, N = 30; see Kolak *et al.* 1999 for Lakes Ontario and Michigan). The high total copper inventories seem a consequence of two factors: 1) basin copper ore deposits naturally scoured along shorelines or submersed ridges (seamounts), and 2) substantial historical anthropogenic inputs.

Across the interior basins of Lake Superior, background copper concentrations in sediments ranged from 37 to 77 µg/g (mean ± 95%CL = 55 ± 5 µg/g), whereas recent surface copper concentrations ranged from 47 to 281 µg/g (164 ± 22 µg/g). The ratio of copper concentration peaks to background values varied from 1.6 to 8.9 (3.1 ± 0.2), indicating substantial anthropogenic inputs. Surface Cu concentrations were lowest in the extreme western and eastern basins (Duluth basin, Whitefish Bay) and highest in mid-lake and mid-eastern basin regions (Kerfoot *et al.* 1994). In the surface 20 cm of sediment, anthropogenic copper ranged between 11-38% of total Cu at central, deep-water sites, but increased to 50-90% close to the Keweenaw Peninsula (Kerfoot *et al.* 1999a, 2002).

Various estimates of copper storage and flux within Lake Superior, some derived from our core surveys, can be used to place the magnitude of the regional Keweenaw Peninsula copper discharge into perspective. Our estimate of total copper flux into sediments (5.0 ± 2.5 µg/cm^2/yr) in Lake Superior is only slightly lower than the value of 5.9 µg/cm^2/yr reported by Kemp *et al.* (1978) from six cores. Since fine-grained sediments cover only about 68% of the lake surface area due to scour zones in shallow areas (mean focusing factor of 1.42), loading values are around 2,790 metric tons total copper per year in permanent sediment regions. Assuming a water copper concentration of 0.7 ng/g (Rossmann and Barres 1988, Nriagu *et al.* 1996), the volume of water in Lake Superior holds 8,470 metric tons of dissolved copper, giving a turnover time of ca. 3 years. An atmospheric flux of 0.3 µg/cm^2/yr (small lake value; Sweet *et al.* 1998, Cook *et al.* 1990) over the entire surface of Lake Superior would contribute 246 tons of Cu per year, or 9% of total net sedimentation. Modern tributary sediments and shoreline erosion contribute an estimated 1,025 metric tons of copper per year (Kemp *et al.* 1978), comparable to the "background" total, but not counting coastline erosion of stamp sand piles. Remobilized Cu from diagenesis (gradient flux from sediment pore waters) adds 0.15 µg/cm^2/yr or 84 metric tons per year returned to the water column (McKee *et al.* 1989). Discharge of water through the outlet, the St. Marys River, estimated at 2,067 m^3/s (Chandler 1964), accounts for only 46 metric tons Cu lost per year.

Against the backdrop of copper cycling, the native copper mining perturbation on the Keweenaw Peninsula was major. Although about 360 million metric tons of stamp sands were discharged around the Keweenaw Peninsula, most of the mass was sluiced into the Keweenaw Waterway (280 Mt into Torch and Portage lakes; Kerfoot *et al.* 1994), creating one of the USA's largest superfund sites (Torch Lake Superfund Site). Around 80 million metric tons were discharged along the Lake Superior shorelines (Kerfoot *et al.* 1994). Assuming an average tailing copper concentration of 0.4%, the amount of anthropogenic copper deposited along the coastline is approximately 320×10^3 metric tons, 3× greater than the entire anthropogenic burden (108×10^3 metric tons) of copper estimated in permanent Lake Superior sediments between 0–20 cm depth. Similar calculations by Kolak *et al.* (1999) give an even greater discrepancy (10×), since their estimates are based only upon comparisons with deep-basin Lake Superior inventories. The important point here is that the majority of the mass is still found along the shoreline, shelf, and coastal regions.

When corrected for sediment focusing, plots of anthropogenic copper inventories reveal a copper-enriched zone that surrounds the Keweenaw Peninsula and that extends northward and northeastward, the latter along the track of the Keweenaw Current (Fig. 4a, focus-corrected 1983 cores). Given the enormous historic input of copper, this pattern is not surprising. Values on or immediately along shelf margins tend to be highly variable, due to intermittent scour ("Scour Zone").

In contrast to the copper patterns, several embayment and coastal regions show locally elevated mercury concentrations (Fig. 4b, crosshatched zones). These coastal anomalies are likely due to historic discharges from several sources: mercury-rich slimicides from pulp and paper mills; mercury from chloralkali plants, municipal incinerators, and coal-burning power plants (e.g. St. Louis Bay, Duluth; Thunder Bay; Peninsula Harbor near Marathon; Rossmann 1999). A few elevated values for mercury in deep-water western basins suggest atmospheric sources in the Silver Bay to Duluth region (taconite mills, see Discussion). There is a very high value at an eastern site (H56A), although sampling is scarce along the NE coastal region, off Terrance Bay, Marathon, and Wawa. The ratio of mercury concentrations in surface sediments to background values varied between 0.9–32.9 (6.4 ± 2.3; CV= 97.8%),

FIG. 4. *Spatial patterns for anthropogenic copper and mercury inventories: a) anthropogenic Cu inventories (contour lines, based on focusing-corrected inventories from the 32 1983 cores) show a halo around the Keweenaw Peninsula (Kerfoot et al. 1999, 2002). Within the previously diagrammed region of inventories > 200 μg/cm² are shown the recent results from KITES sampling (squares), suggesting that the region of > 200 μg/cm² is more restricted than indicated by the focusing corrected 1983 cores. However, there is still a clear "halo" around the Peninsula. Inventory values are marked by squares, with the hollow symbols indicating values similar to remote lakes, whereas solid symbols indicate larger values. b) anthropogenic mercury illustrates a more scattered spatial pattern, with several coastal "hot spots" (cross-hatched regions, see Rossmann 1999 for discussion of sources). Seven levels of Hg sediment inventories (ng/cm²) are distinguished; the first two (hollow circles) are in the range of remote lakes, whereas solid symbols indicate enrichment above remote lake values. The Hg inventories are not focusing corrected. The cross-hatched regions denote areas where enriched inventories are common, generally near past or present industrial centers.*

with a mean ratio more indicative of industrial sites (5.0–6.3, eastern Europe), rather than remote regions (remote 2.0–3.4, Fitzgerald *et al.* 1998, Hudson *et al.* 1995). The relatively high concentrations of mercury found off the Keweenaw Peninsula posed a dilemma to us, for no obvious paper mills, chloralkali, or large power plant sources were present, and mercury had not previously been recognized as an ancillary component of copper ore.

Mercury/Copper Correlation around the Keweenaw Peninsula

When we plotted anthropogenic metal inventories from deep-water Lake Superior to interior Keweenaw Waterway sites, silver and mercury values were strongly associated (Fig. 5a, r^2 = .839). The association was also strong between mercury and copper (Fig. 5b, r^2 = .517). The correlation remained significant when Lake Superior and Keweenaw Waterway values were separated into two independent groups (Lake Superior, r = 0.445, N = 43, $p < .01$; Keweenaw Waterway, r = .518, N = 20, $p < .05$). The high correlation between silver and copper inventories suggested that regional geological ("rock") sources were contributing to the association, since silver is not cycled through the atmosphere.

The Ponar survey of Keweenaw Bay surface sediments (Fig. 2c) provided an independent verification of pattern, for there was again a high association (Fig. 6a, r^2 = .639) between Hg and Cu in surface sediments. As in the inventory survey, a significant, non-zero regression intercept (Table 2) suggests that local anthropogenic enrichments of mercury are superimposed upon remote regional atmospheric inputs.

Despite the linear trend in the above inventory and surface regressions, the increase in Hg is not equal to the increase in Cu (slope in Fig. 5b is 0.700, in Fig. 6a it is even lower, 0.383). Because the slopes are not equal to 1.0, if the anthropogenic Hg:Cu ratio is plotted as a function of the anthropogenic Cu inventory, a higher ratio and a nonlinear relationship is evident as one moves into open lake sediments (Fig. 6b). That is, dispersal of particles which contain a fixed Hg:Cu ratio could not explain the observed Hg:Cu association. There are two possibilities, which we have difficulties distinguishing between. First, there could be a local atmospheric source (e.g., smelter release) superimposed upon particle spread. In this case, mercury could disperse further than Cu (superimposed dispersal diagram, Fig. 6b) and this phenomenon would help explain the observed
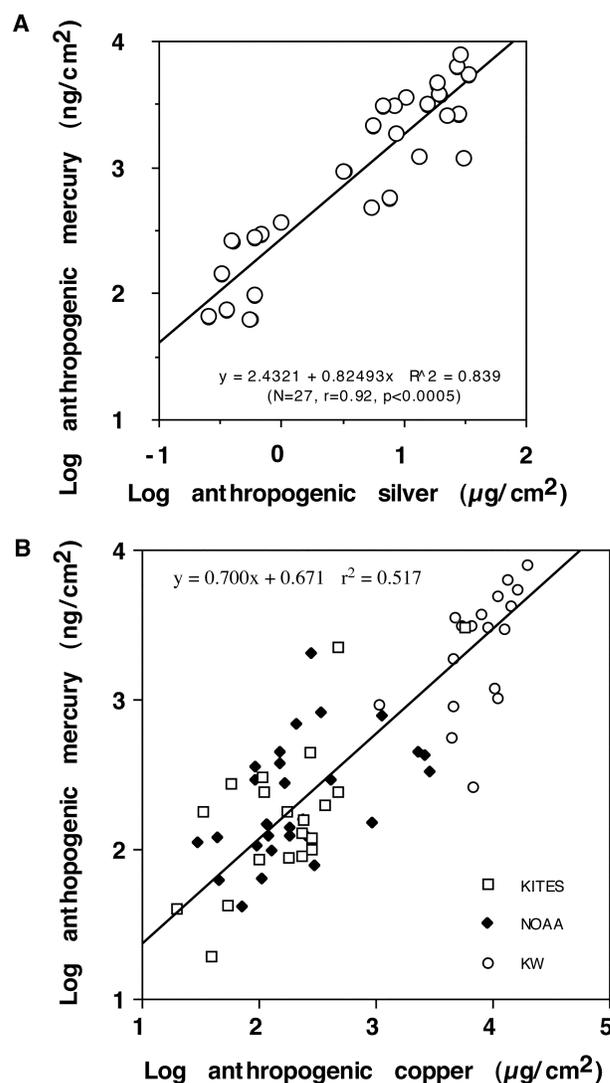
FIG. 5. Correlation between anthropogenic copper, silver, and mercury inventories around the Keweenaw Peninsula: a) correlation between silver and mercury inventories; b) correlation between copper and mercury inventories. Values plotted on log-log scale. For copper/mercury plot, Lake Superior, KITES, and Keweenaw Waterway sites are distinguished by different symbols. Note the 3-4 order of magnitude range of values. Equations and coefficients of determination given for regressions.

increase. Differential dispersal of elements from smelter sites is not unusual (Sterckeman *et al.* 2002). A second interpretation is that long-distance regional deposition of atmospheric Hg could be secondarily superimposed upon the local pattern as another source, which would also explain the enriched Hg:Cu ratio in off-shore waters. Significant non-zero
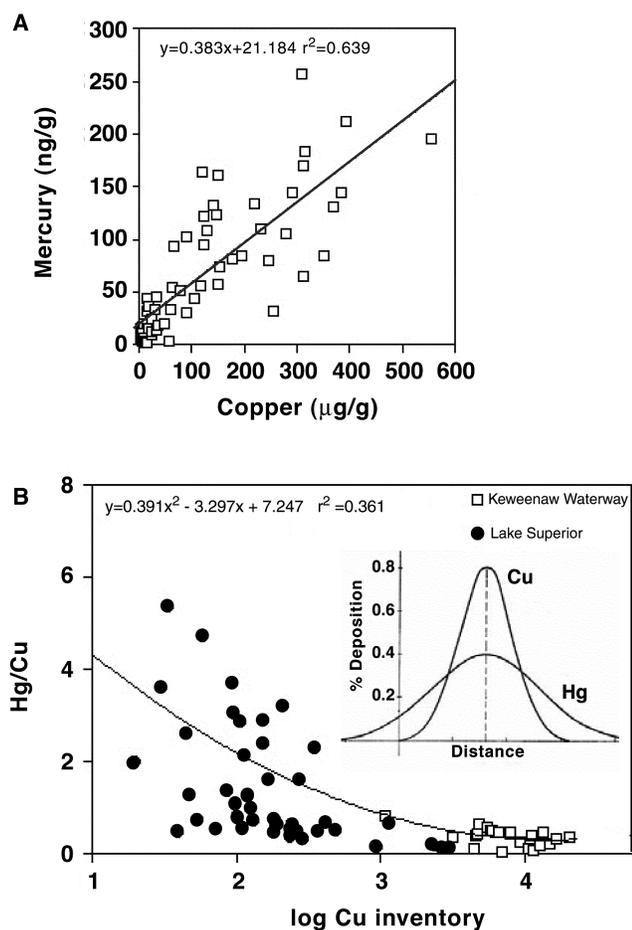
FIG. 6. *Ponar survey results and Hg/Cu ratios: a) Hg and Cu concentrations in Keweenaw Bay ponar samples, showing that correlation carries over in surficial sediments (note non-zero intercept). A full regression analysis is given in Table 2. b) plot of Hg/Cu ratio for anthropogenic inventories versus log Cu inventory. Data points from Keweenaw Waterway (squares) and Lake Superior (solid circles) are distinguished. Elevated ratios might result from differential dispersal of Cu and Hg from local sources (stamp sands, smelters) or superimposition of Hg from two sources (local, regional). Insert illustrates how a different dispersal pattern versus distance (Cu, less; Hg, 2X greater) will produce different ratios.*

intercepts in inventory and concentration regressions (Fig. 5b, 24.7 ng/cm^2; Fig. 6a, 21 ng/g) suggest a secondary, long-distance source of mercury superimposed upon the local dispersal pattern. A third possibility is that both processes (local smelter discharges and remote deposition) could be involved in producing the non-linear relationship.

TABLE 2. Regression of Hg on Cu concentration, Ponar samples from Keweenaw Bay, Lake Superior (N = 59; r^2 = 0.639; Cu mean, 128.5 µg/g; Hg mean 70.4 ng/g). Regression constants given first, followed by analysis of variance.

Effect	Coefficient	Std Error	t	P
Constant	21.2	6.9	3.0	0.003
Slope	0.383	0.038	10.1	0.000

Source	SS	df	Mean Sq	F-ratio	P
Regression	144876	1	144876	101.1	0.000
Residual	81696	57	1433		

Historic Details of Copper/Mercury Concentrations and Fluxes

Low sedimentation rates in deep-water regions of Lake Superior make historical details difficult to unravel. The records are too compressed and reworked by bioturbation at deep Lake Superior locations (Fig. 7, LSDH, EV-26A) to reveal historical trends. However, as we approached mainland sites, higher deposition rates provided stratigraphic insights into the Keweenaw mining perturbation. Background concentrations were around 30–50 µg/g for copper and 10–25 ng/g for mercury. Off mill discharge sites along the Keweenaw Peninsula, a buried copper-mercury peak was present (On-210, MI) and pronounced in Keweenaw Bay (KT, LB). Concentrations of copper and mercury became elevated and stratigraphically correlated, rising to 150–250 µg/g for copper and 100–120 ng/g for mercury in the Keweenaw Trough. The terminal, L'Anse Bay portion of Keweenaw Bay had copper concentrations beyond 700–800 µg/g and mercury concentrations beyond 100 ng/g.

We suspect that the peak concentrations in Keweenaw Bay mark the historic "slime clay" fraction of stamp mill discharges (Wolverine and Mohawk Mills at Gay, Mass Mill north of Baraga) that moved out into Lake Superior, i.e., direct particle settling. Discharges from the Mass Mill site probably funneled into L'Anse Bay, rather than dispersing more evenly out into Keweenaw Bay. Concentrations of both copper and mercury declined after the buried peak, relaxing to values (100–150 µg/g Cu, 50–60 ng/g Hg) characteristic of open-water Lake Superior sediments. In L'Anse Bay (LB), surface Cu concentrations remained elevated above Lake Superior open-water norms, whereas Hg con-
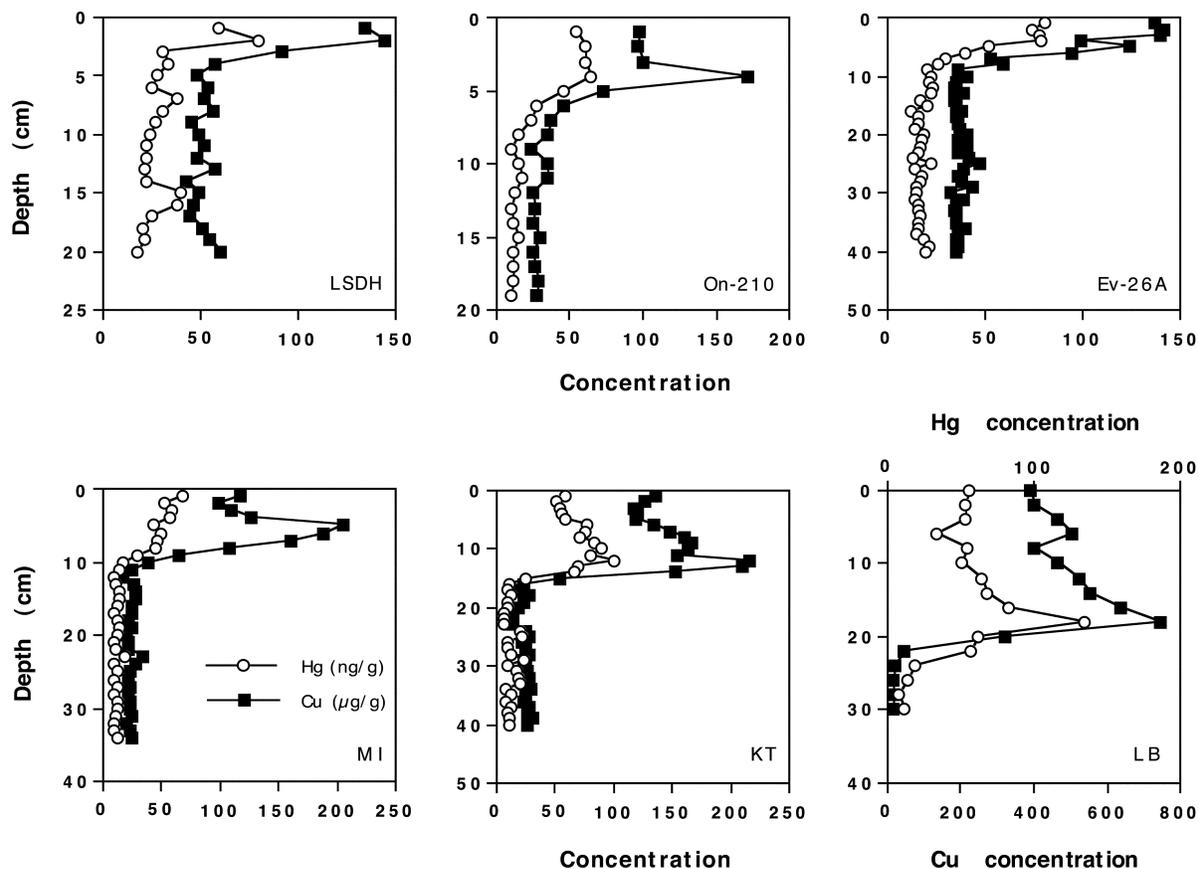
FIG. 7. *Copper/mercury profiles in KITES cores, ranging from deep-water (LSDH, On-210, Ev-26A) series to a Keweenaw Trough series (MI, KT, LB) that ends in L'Anse Bay (mercury ng/g, copper μg/g; see Fig. 2a for site locations).*

centrations at some sites have relaxed back to open-water values.

In the Keweenaw Waterway, high mass deposition rates, radioisotope studies, and varve counts permitted reconstruction of detailed flux chronologies. Moreover, the broad spatial coverage within the present study revealed site-specific profiles that emphasized the discharge histories of nearby individual mills and smelters.

Sediments in the Keweenaw Waterway showed elevated levels for copper and mercury (Table 1), despite low background copper and mercury concentrations comparable to open-water Lake Superior values (background copper 41 ± 4 μg/g, mercury 39 ± 5 ng/g, N = 80). Surface copper values ranged between 90–1,734 μg/g with a mean of 975 ± 201 μg/g (N = 18), whereas surface mercury concentrations ranged between 96–512 ng/g with a mean of 313 ± 66 ng/g (N = 18). The anthropogenic contribution was uniformly high (Table 1), varying between

71% (site PB) to 99% (site TWL) of total copper. All cores had buried copper and mercury concentration peaks, with enrichment ratios that ranged between 10–131 (mean 44 ± 18, N = 14) for copper and 1.2–17.7 (mean 5.9 ± 2.8, N = 18) for mercury, again indicative of industrial areas. Highest peak mercury concentrations were recorded at HAN (1,781 ng/g), CG (1060), DH (1010), PL-2 (960), SP (816), PL-1 (799), and CC (680). Mercury inventories (Table 1) varied from 298 ng/cm² (site SEWL) to 8,432 ng/cm² (site CG), with the anthropogenic fraction accounting for 58% (site PB) to 95% (site CG). In contrast to the broad distribution of copper contamination, peak mercury concentrations and inventories were near or downwind from smelter locations.

In the 19 Keweenaw Waterway profiles, surface copper flux ranged from 3–57 μg/cm²/yr (mean 26 ± 8; CV= 57%). All cores had buried peaks in copper flux (Fig. 8). Copper values began to rise in the late 1800s, reached a maximum between 1900-1920,
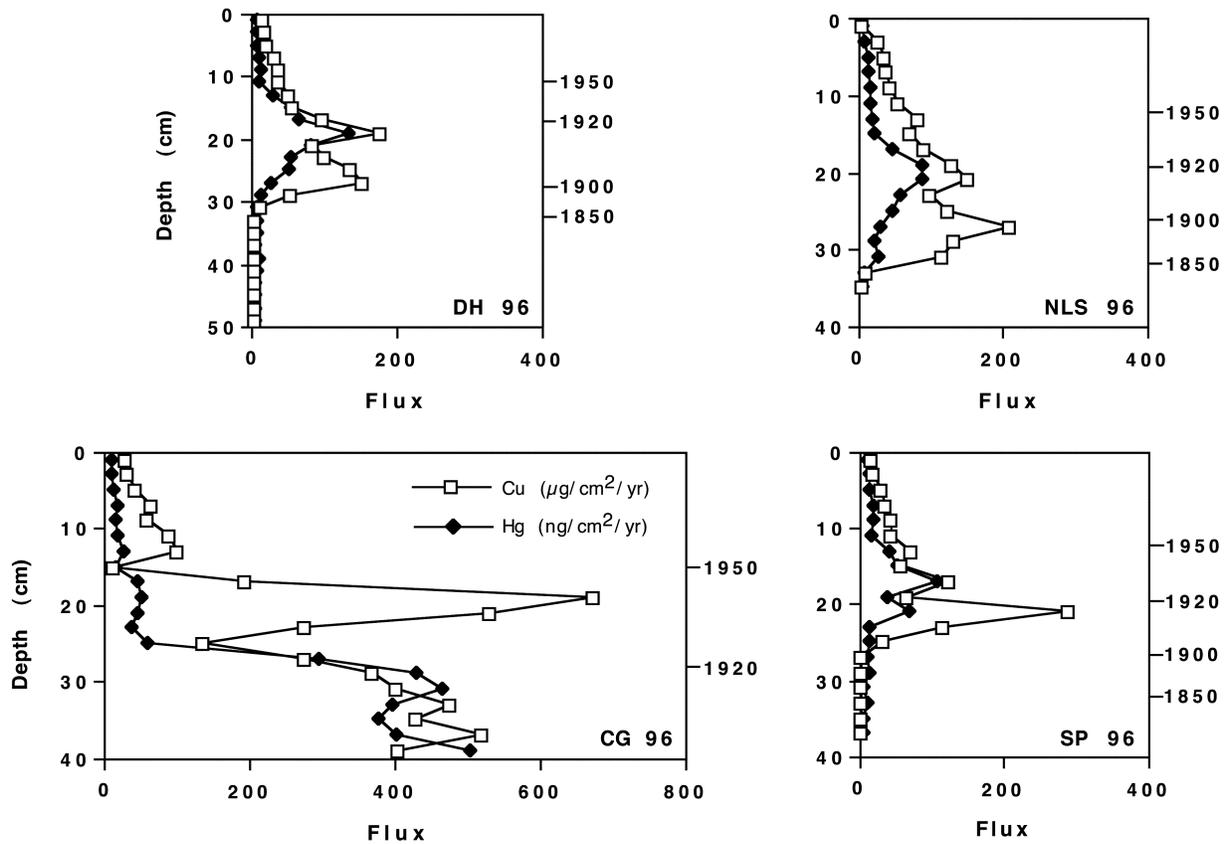
FIG. 8. *Comparison of copper and mercury flux profiles at several Keweenaw Waterway sites. Flux values are plotted on the same x-axis scale. Dates are given to the right of profiles, based on the position of annual slime clay varves cross-correlated with ^{210}Pb and ^{137}Cs profiles (see Fig. 3; also Kerfoot* et al. *1994, Kerfoot and Robbins 1999).*

showed a secondary peak between 1938-1948 (World War II), and then declined until the present. Highest Cu fluxes were at CC (616 µg/cm²/yr), CG (673), and DB-1 (669), all sites close to either stamp sand piles or smelters.

Although copper and mercury concentrations and fluxes were correlated to highly correlated at most sites, the spatial and temporal patterns for mercury contained distinguishing features. All cores showed mercury fluxes rising initially with copper mining activity, and declining recently, after the close of stamp sand and smelting activities. The detailed pattern of Hg peak fluxes did not correspond exactly with the peaks for Cu fluxes (Fig. 8), known to closely match the history of stamp sand discharges (Kerfoot *et al.* 1994, Kerfoot and Robbins 1999). Instead, Hg flux consistently peaked between 1900–1920, during the maximum period of copper

processing and local smelter activity (Kerfoot *et al.* 1999a, 2002).

Initially mass copper was shipped to Detroit or eastward for smelting. Michigan Technological University (MTU) Archive records document that four of the five smelters opened between 1885–1904, whereas several closed in the early 1930s, reopening later for copper recycling. Spatially, peak Hg fluxes occurred at CG (463 ng/cm²/yr), HAN (445), IR (270), SLS (284), and CC (130), again all close to or downwind from smelter sites (Fig. 2b). Thus both mercury concentrations and fluxes were high for Keweenaw Waterway sediments, with strong indications of smelter releases superimposed upon stamp sand discharges. Surface fluxes for total mercury (Table 1) ranged from 2–41 ng/cm²/yr (mean 11 ± 7 ng/cm²/yr; CV = 113%; N = 14), remaining elevated above background levels.

Mercury Source Revealed

There is no evidence (company records, MTU Library Archives) that amalgamation extraction techniques were practiced on native copper lodes. Rather, separation of copper from ores relied on simply crushing the rock under stream-driven stamps, followed by gravity separation in jigs and "slime" separation on Wilfley tables (Benedict 1955). Finding that mercury was not imported for routine copper and silver processing, we focused our attention on the mineral constituents of the ore.

Copper was present in all four poor rock samples and ten stamp sand samples at relatively high values, averaging 2,295 ± 599 and 4,364 ± 900 µg/g, respectively. Silver was also present, averaging 2.4 ± 0.6 and 3.2 ± 0.5 µg/g, respectively, close to the 1,000:1 ratio considered typical for regional native copper ores (Olson 1986). Mercury concentrations in crushed samples of the parent basalt rock were very low, ranging from 2 to 5 ng/g. "Poor rock" and "stamp sand" samples contained mercury, although concentrations were relatively low, averaging 85 ± 25 and 48 ± 12 ng/g, respectively. In stamp sand samples, there was a weak, but significant, inverse relationship between grain size and concentration ($r = 0.541$, $p < 0.0005$, $N = 43$), probably reflecting adsorption of Hg onto the iron-rich "slime clay" fraction. The enrichment with small particle size is important because the finest size fractions, the slime clay fractions which average between 100-200 ng/g mercury, are more likely to be transported further from shoreline stamp sand piles by wave action. This enrichment would account for much of the generally elevated mercury concentrations in the Keweenaw Waterway and Keweenaw Bay.

Direct tallies from major mill inventories document that at least 345 million metric tons of stamp sands were discharged by large operations. An alternative approach, using the average "grade" of rock (g Cu/kg rock; Butler and Burbank 1929) and total copper produced from company records, gives an estimate of 364 million metric tons of stamp rock processed by large operations. Multiplying the mean concentration of mercury by the estimated amount of stamp sand discharged suggests that 17–18 metric tons of mercury were contributed to sediments by native copper mill operations alone. However, stamp sands were not the sole, nor even the largest, source of mercury.

Samples of native copper and silver ores from 29 abandoned Keweenaw Peninsula mines were analyzed for copper, mercury, and silver (Fig. 9a, Table 3). Ore samples were selected which contained high amounts
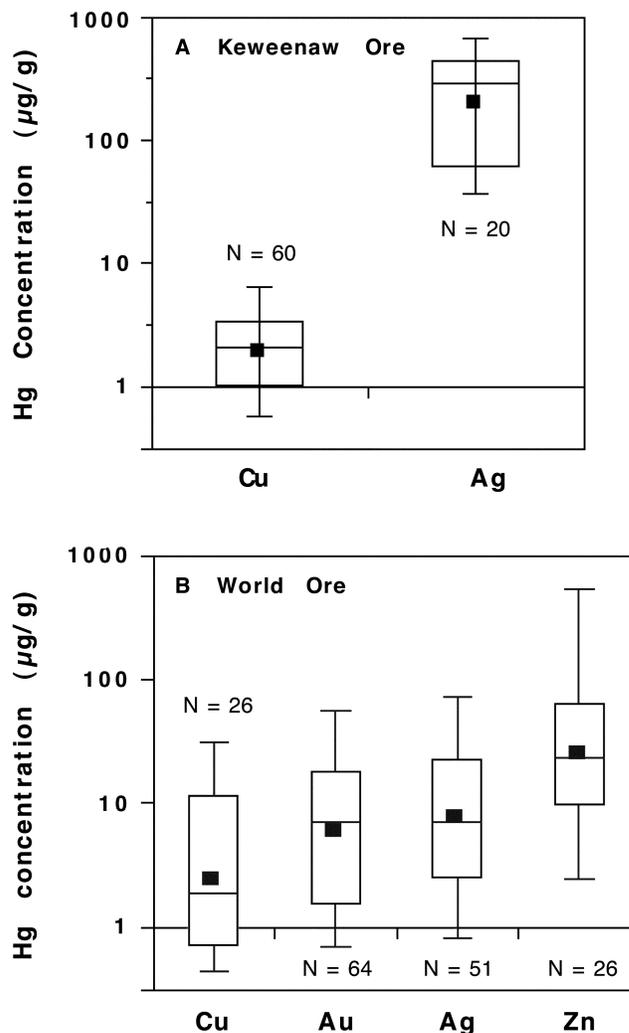

FIG. 9. *Mercury concentrations in ore samples: a) concentrations from Keweenaw native copper and silver ores; b) concentrations in copper, silver, gold ores and the mineral sphalerite (ZnS) from around the world. Log transformation used to normalize variance with sample sizes given next to Box and Whisker diagrams. Horizontal lines on the Box and Whisker diagrams indicate 75th percentile (top quartile), 25th percentile (bottom quartile), and 50th percentile (median). Whiskers extend from 10th percentile (bottom) to 90th percentile (top); solid squares indicate modes.*

of metal (copper or silver or both). All samples tested were found to contain mercury in relatively high trace concentrations, e.g µg/g, orders of magnitude above stamp sand or poor rock concentrations.

Mercury concentrations in Keweenaw Peninsula native copper varied between 0.1–47.1 µg/g, with a

TABLE 3. *Concentrations of metals in Keweenaw poor rock, stamp sands and various ores (N = sample size, CV = standard deviation/mean).*

Ore Type	Element	N	Range	Mean ± 95 C. L.	CV (%)
Poor Rock	Cu (µg/g)	32	151–6,457	2,295 ± 599	74
	Ag (µg/g)	32	0.3–7.0	2.4 ± 0.6	73
	Hg (ng/g)	32	9–281	85 ± 25	82
Stamp Sands	Cu (µg/g)	68	366–16,163	1,364 ± 900	85
	Ag (µg/g)	68	0.6–8.7	3.2 ± 0.5	69
	Hg (ng/g)	68	2.8–265	48 ± 12	101
Copper Minerals	Hg (µg/g)	24	0.5–6.5	2.4 ± 0.6	65
Native Copper	Hg (µg/g)	60	0.1–47.1	3.9 ± 2.1	203
Half-breed	Hg (µg/g)	10	0.7–981.3	154 ± 198	204
Native Silver	Hg (µg/g)	30	34–2,548	394 ± 187	130

mean of 3.9 ± 2.1 µg/g. Mercury concentrations in half-breeds (mixtures of copper and silver) were elevated and highly variable, ranging between 0.7–981.3 µg/g (mean = 154.0 ± 197.6 µg/g). Native silver from eight lodes contained two orders of magnitude higher mercury concentrations than native copper, ranging between 34–2,548 (mean 394.3 ± 186.7) µg/g. Thus mercury was intimately associated with the copper, copper-silver (half-breed), and silver metal samples, suggesting that it occurs in a natural amalgam state in solid solution, facilitated by the presence of silver.

Further tests run on other mineral forms of copper found with gangue minerals in Keweenaw deposits also revealed the presence of trace mercury, with values that ranged between 0.5–6.5 (mean 2.4 ± 0.6) µg/g (Table 3). Appreciable concentrations of Hg were detected in local bornite (Cu_5FeS_4, 2.5 µg/g, SD = 1.4, N = 3), chalcocite (Cu_2S, 3.2 µg/g, SD = 1.9, N = 9), and domeykite (Cu_3As, 1.7 µg/g, SD = 0.8, N = 9). Exceptionally high values were found in the zinc mineral sphalerite (190.0 µg/g, SD = 54.6, N = 6), rivaling values from silver ores.

Large amounts of metal ore were smelted at sites along the Keweenaw Waterway, at Portage and Torch lakes (Portage Lake Smelting Works, later renamed the Detroit and Lake Superior Smelter 1860–1905; Dollar Bay Smelting Works 1898–1919; Quincy Smelter 1898–1931; Michigan Smelter 1903–1945, at Portage Lake; Calumet and Hecla Smelter, at Torch Lake 1885–1948). Multiplying the mean mercury concentration times the amount of metal processed gives a total of about 20–24 metric tons of Hg released during smelting, with peak values reaching 400-600 kg/yr. Thus smelting probably contributed the largest amount (ca. 59%) of the mercury liberated from processed ore.

The yearly atmospheric discharge of Hg from native copper smelters is lower than the amount (635 kg/yr) estimated from the modern-day White Pine Smelter, before it closed in 1995 (Michigan DNR, quoted by NWF). However, our native copper value does not include smelting release of mercury from gangue or associated minerals, which would substantially increase the projected amount. The relatively large total release from smelting operations explains why the high mercury inventories of the Keweenaw Waterway sediments are traceable back to local smelter sites. In all, we estimate that at least ca. 42 metric tons of mercury (smelting + stamp sands) were released from native copper mining operations. Of this total, only about 10 metric tons is contained in the fine sediments of the Keweenaw Waterway (inventories from Fig. 2b core sites x area of Waterway; Harting 1999), suggesting that substantial amounts were lost to the atmosphere (volatilized as Hg° during smelting; or volatilized from stamp sand piles and sediments after deposition).

To place the above release values into a regional context, current IJC estimates for yearly total Hg atmospheric inputs to Lake Superior are 0.82 metric tons/yr, with 0.32 metric tons/yr of the total coming from watershed sources (Hurley *et al.* 2001). Our 1983 samples suggest that the surface 20 cm of sediments in Lake Superior contain about 342 metric tons of mercury, of which 51% or 174 metric tons is anthropogenic. Based on values from the top 2 cm of the 1983 sediment cores (ca. 15 yrs), 29 metric tons of mercury are stored (ca. 1.9 metric tons/yr). The 1.9 metric tons/yr estimate nearly doubles the IJC estimate of modern-day total loading (Rossmann 1999), suggesting greater historical inputs than previously suspected. Of this, 22 metric tons or 74% is anthro-

pogenic (Rossmann 1999). We suspect that, as in the local case of Keweenaw Copper processing, mining activities in the watershed have contributed substantial amounts of mercury to regional cycling, accounting for the 5–7 fold discrepancy in inventories between Lake Superior and small lake sediments.

Despite the elevated concentrations in Keweenaw Waterway sediments, we feel obligated to point out that mercury concentrations in open-water Lake Superior surface sediments are relatively low (mean 0.18 μg/g, Rossmann 1999), compared with recent findings from Lake Erie (western basin 0.65 μg/g, eastern basin 0.25 μg/g; Marvin *et al.* 2002) and Ontario (Kingston basin mean 0.47 μg/g; Niagara basin mean 0.66 μg/g; Marvin *et al.* 2003). The additional mercury in Lake Superior seems to show up along coastal margins, as in the case of the Keweenaw Peninsula.

DISCUSSION AND CONCLUSIONS

Because mercury was present as a natural amalgam in copper-silver ores and associated gangue minerals in the Keweenaw Peninsula, copper mining contributed mercury to the Keweenaw Waterway and created a detectable halo that extends out into Lake Superior. Since more mercury was released from smelting activity than from stamp sand discharges, the highest concentrations of mercury are found around smelter sites, mostly in the Torch Lake and Portage Lake portions of the Keweenaw Waterway. However, distinguishing between differential dispersal of metals from smelter sites and the nuances of local versus long-distance sources in deep-water Lake Superior sediments will require application of more sophisticated approaches, perhaps mercury and copper stable isotope techniques (Zhu *et al.* 2000). Yet recognition of trace mercury in regional ore sources has implications for other mining contributions in the Lake Superior watershed, as well as for global mining activities. Recall that the Keweenaw Peninsula is only one of many intensively mined regions around the Lake Superior watershed (Fig. 1).

Determining regional mining contributions (Canadian and USA sides of the watershed) runs into a curious discrepancy in acknowledged mercury sources (Fig. 10). The 1997 U.S. EPA Report to Congress hardly mentioned mining releases in the U.S., yet recent Canadian revisions of mercury atmospheric sources list mining as the chief contributor in Canada and second in the U.S., behind coal-burning electric power generation and incineration (UNEP 2002; Environment Canada 2000). To quote
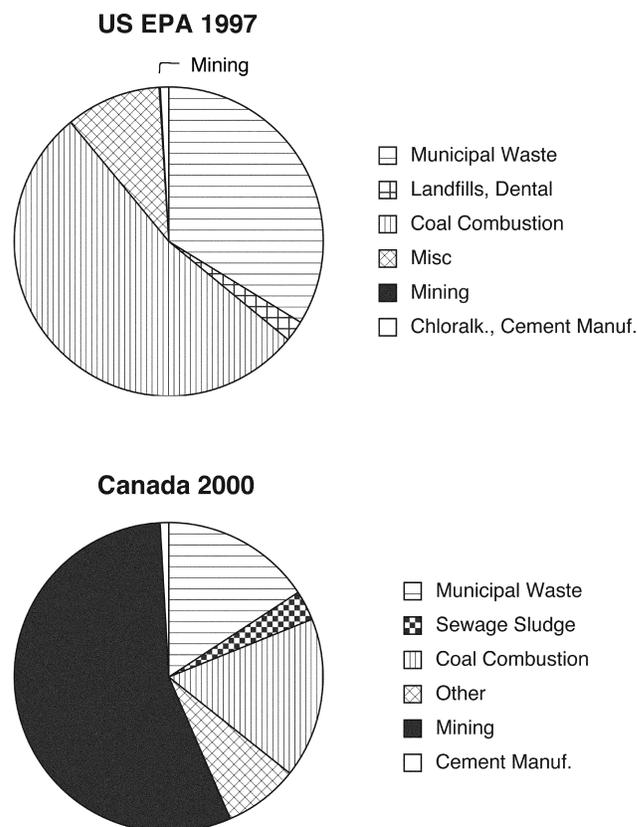

US EPA 1997

Municipal Waste
Landfills, Dental
Coal Combustion
Misc
Mining
Chloralk., Cement Manuf.

Canada 2000

Municipal Waste
Sewage Sludge
Coal Combustion
Other
Mining
Cement Manuf.

FIG. 10.   *Comparison of sources for atmospheric Hg discharges. Figure contrasts emission sources from Environment Canada (2000) versus the U.S. EPA Report (1997) to Congress. Values are presented as percentages in a pie diagram. Note the very small value (~0.1%) for mining in the 1997 EPA Report.*

Environment Canada (2000), ". . . the largest industrial source of mercury emissions in Canada is the nonferrous (primary base-metals) industry, which, in 1995, contributed almost 50 percent of the total 11 tonnes of mercury emitted to the atmosphere by selected industrial sources."

In 1998, EPA's Toxics Release Inventory program began to include metal and coal mining, along with electricity generation, in the reporting structure. At an EPA-sponsored 2000 conference in San Francisco ("Assessing and Managing Mercury from Historic and Current Mining Activities"), the agency began to tackle mining-related inputs. Traditional concerns centered on import of mercury for amalgam extraction of gold or silver from ores (Nriagu 1994). Between 1840–1930, the amount of mercury utilized by precious metal mining and prospecting in the U.S. and Canada was enormous (e.g., 13,500 metric

tons in California; 6,750 metric tons at the Comstock Lode, Nevada; Nriagu 1994, Lindberg *et al.* 2000). "On-site" amalgamation in miner's pans released about seven to thirty grams of mercury for every metric ton (10^3 kg) of gold ore processed (Eissier 1898, Buhler *et al.* 1973). Mercury also was added to sluice boxes or placed on copper plates in contact with washed sediments (Fountain 1992, Nriagu 1994). On the U.S. side of the Lake Superior watershed, examples included the Ropes Gold Mine at the Deer Lake Area Of Concern (Fountain 1992, Kerfoot *et al.* 1999a), whereas on the Canadian side, they included the extensive gold fields east of Lake Nipigon, near Marathon, and around Wawa (Kerfoot and Nriagu 1999). The Nipigon region alone (Beardmore/Geralton and Tashota/Onaman Belts) produced 116 metric tons of gold between 1934–1966 (Mason and McConnell 1983). Regional import of mercury declined when the mining industry converted from amalgam extraction to cyanide leaching in the 1930s.

However, the transition to cyanide leaching did not end mercury emissions as techniques produced concentrates with enriched naturally-occurring mercury. In two Bureau of Mines investigations of mercury contamination during cyanide leaching, Sandberg *et al.* (1984) and Simpson *et al.* (1986) stated that "gold and silver ores typically contain other metals such as mercury and a variety of base metals." They reported Hg concentrations that ranged between 3–31 µg/g from five gold lodes studied in Nevada. Both investigators voiced concern that Hg in concentrates from cyanide leaching might pose health problems. In 1998, the EPA Toxic Release Inventory for the first time included mercury release data from U.S. gold mines. For 1999, over 6.5 metric tons per year of mercury air emissions were recorded from Nevada gold mines alone with individual plant emissions ranging between 500–700 kg/yr (e.g., ca. 550 kg, Twin Creeks Mine; ca. 630 kg, Betz-Post Mine). By 2001, comprehensive reporting from EPA Region 9 emphasized the magnitude of mining contributions (Fig. 11a). For that year, mercury releases were dominated by mining (land: gold 1,886,901 kg;

FIG. 11. *On-site mercury releases (atmospheric): a) in 2001 by source category, U.S. EPA Region 9 (Arizona, California, Hawaii, Nevada, Pacific Islands). Scale is log-transformed. b) Preliminary estimates for 1994 precious (Au), iron (Fe), and base-metal (Zn, Cu) contributions, Lake Superior watershed (see Table 4). Scale is not log-transformed.*
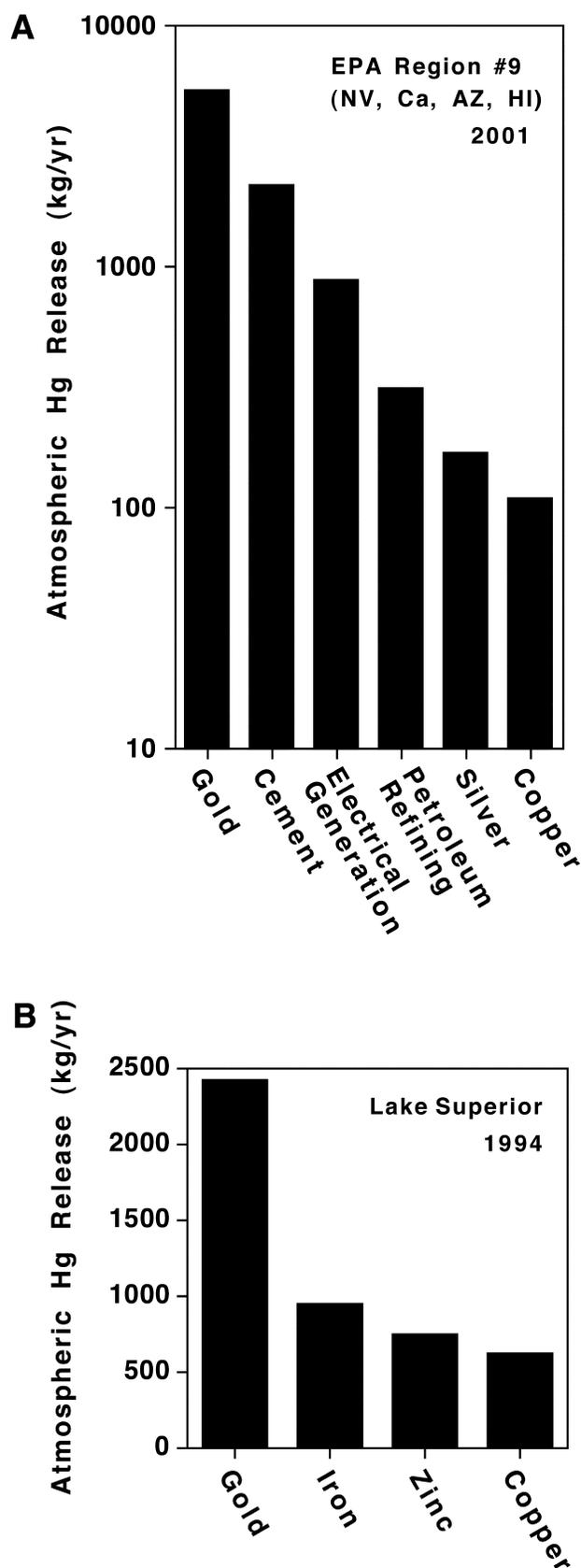
TABLE 4.   Mercury release estimates (preliminary) from mining for the year 1994, Lake Superior water-shed. Site estimates of Canadian ore milled and metal produced are taken from Jen and McCutcheon (1995). The mercury emission factor for Hemlo operations is calculated from the mercury:gold ratios in Golden Giant concentrates (Hendriks and Chevalier 2001), whereas the iron pellet value comes from Jiang et al. (2000). The White Pine mercury release estimate is from MDNR, cited in LSBP (2002). For copper and zinc mines, emissions are based on 4.0 µg Hg/g for copper ore, 110 µg Hg/g for silver ore, and 10.0 ug Hg/g for Geco zinc (Schwartz 1997).

| Mine | Ore Milled (10^3 tonnes) | Metal Produced | | | | Emission Factor | Release(kg) |
		Copper (tonnes)	Zinc (tonnes)	Silver (kg)	Gold (kg)		
Golden Giant	1,107	—	—	737	13,900	.080 g Hg/g Au	998
David Bell	465	—	—	150	6,012	"	432
Williams	2,303	—	—	815	13,851	"	995
Winston Lake	358	3,419	50,244	6,887	307	—	557
Geco	799	16,056	19,476	29,752	69	—	202
White Pine	—	43,200	—	—	—	(MDNR)	635
Taconite Pellet	47.35×10^9 kg (Pellets)	—	—	—	—	7.48 ng Hg/g (Pellets)	354
Wawa Plant	700	—	—	—	—	(IJC)	600

silver 23,162 kg; copper 12,958 kg; atmospheric: gold 5,473 kg; silver 171 kg; copper 111 kg). Some of the more profitable Nevada operations invested in capturing mercury as a secondary product (Jones 2000, Wickens 2000), a practice that will greatly reduce future atmospheric emissions.

The Lake Superior watershed (Fig. 1) is also an intensively mined region that has many similarities with Region 9, but reporting of mercury release has been voluntary or nonexistent. Our assays on voucher specimens from Greenstone Formation ores in Ontario verified a widespread incidence of trace mercury in ores (silver mines, 13.3 ± 19.6 µg/g, N = 12; gold mines, 6.1 ± 7.7 µg/g, N = 10; also see Kerfoot *et al.* 2002). During the past 20 years, 25% of Canadian gold production has come from the Schreiber-Hemlo Greenstone Belt. At present, three mines exploit the Hemlo gold deposit (Williams, Golden Giant, and David Bell mines), processing ores laced with cinnabar and mercurian sphalerite (Michibayashi 1995; Powell and Pattison 1997; Tomkins *et al.* 2004), similar to Nevada mines. At the Golden Giant Mine, initial plans were to cyanide leach, utilize a Knelson Concentrator, and to smelt the concentrate on site. Some 8.4 million metric tons of ore were processed between 1985–1996, when according to Hendriks and Chevalier (2001), "This procedure worked well until large amounts of liquid mercury was (sic) found in the ducting from the induction furnace." Mercury in concentrates ranged between 1 ppm to 19%, with a mean ± 95% C.L. of 6.7 ± 1.8% (N = 29, data from Hendriks and Cheva-

lier 2001). Fearing for employee safety, attempts to refine the concentrate on site were halted and the material was shipped elsewhere for refining (1996). Knowing the ratio of Hg to Au in the concentrate allows us to calculate an emission factor for the Hemlo contribution and to estimate basin-wide atmospheric release of Hg (Table 4). We present values for the year 1994 as an example, using milled tonnage and metal production estimates from Jen and McCutcheon (1995). As in EPA Region #9, gold mining dominates atmospheric release categories with 2,170 kg Hg/yr, followed by iron and base metal (zinc, copper) mining (Fig. 11b, Table 4). To place these estimates into perspective, previous LaMP estimates of early 1990s mercury emissions from mining within the watershed were 1,516 kg/yr, with fuel combustion at 263 kg/yr and incineration at 86 kg/yr (LSBP 2002). Although our calculations for mining emissions are preliminary, we feel they begin to explain the several-fold difference in sediment mercury inventories found between isolated small lakes and Lake Superior.

Trace mercury concentrations are found in copper, silver, gold, and massive metal ores worldwide, with especially high concentrations in the mineral sphalerite, the prime source of zinc ore (Fig. 9b; Kerfoot *et al.* 2000, 2002; list of assay results can be obtained from the authors, with a copy deposited at the Seaman Mineral Museum, MTU). Chief among recognized mercury trace occurrences are hot-spring gold-silver deposits, sediment-hosted gold deposits, copper and zinc-rich massive sulfide deposits, poly-

metallic base metal replacement deposits, volcanogenic uranium deposits, antimony deposits, Franciscan-type and bedded manganese deposits, and bedded barite deposits (Rytuba 2000). In massive sulfide deposits, solid solution replacement of zinc by mercury in sphalerite helps explain trace mercury values that range between 1–998 µg/g (Jonasson and Sangster 1975, Schwartz 1997). However, for zinc release in the Lake Superior basin, we used the rather conservative estimate of 10 µg/g listed for the Geco Mine (three samples, Schwartz 1997), rather than the weighted mean value of 123 µg/g (N = 248) for worldwide zinc deposits (Schwartz 1997) or our own worldwide estimate of 117 ± 57 µg/g (mean ± 95% C.L., N = 70).

Estimating total historic mercury release in the Lake Superior watershed by mining is difficult, since so many operations followed local boom and bust cycles (Kerfoot *et al*. in prep.). In the absence of site-specific atmospheric mercury emission records, reconstructing the amount of historic release probably requires an indirect approach, as accomplished recently for Mexico by Acosta-Ruiz and Powers (2003). Documenting impacts on sediments is more straightforward. The Canada Centre for Inland Waters (CCIW) has recently conducted surveys of sediments in Lakes Ontario and Erie (Marvin *et al.* 2002, 2003), yet the last surveys of Lake Superior Canadian waters date from the 1980s. We would like to encourage additional detailed survey efforts along the Marathon, Wawa, and Sault Ste. Marie coastal regions to determine if the high values at H56A are anomalous, or indicative of elevated coastal mercury inventories off Canadian mining locations.

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