Mercury In Metal Ore Deposits: An Unrecognized, Widespread Source To Lake Superior Sediments

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Abstract
Mining operations have worked the rich mineral resources of the Lake Superior Basin for over 150 years, leaving industrially impacted regions with tailing piles and smelters. In Lake Superior sediments, mercury and copper inventories increase towards shorelines and are highly correlated with each other and with silver inventories, suggestive of fine particle transport from terrigenous sources. In the Keweenaw Peninsula region, high copper, silver, and mercury inventories can be traced back to shoreline tailing piles, the parent ores and to smelters. Mercury occurs as a natural amalgam in native metal (copper, silver, gold) deposits and was liberated as volatile Hg^o during on-site smelting. Stamp mills discharged 0.5 billion metric tons of "stamp sand" tailings, while smelters refined five million tons of native copper. Although silver-enriched native copper deposits in the Keweenaw Peninsula contain relatively high amounts of mercury, mineral-bound mercury is commonplace in Canadian and U.S. Greenstone Belt metal ores. Moreover, a survey of mine samples from around the globe documents worldwide occurrence of mercury as a trace metal in massive base metal ore bodies.

Lake Superior Cores. Offshore sediment core samples were provided by the NOAA Great Lakes Environmental Research Laboratory (GLERL), from cores originally collected at 32 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 broadly over several offshore and nearshore sedimentation basins: Duluth Basin, Thunder Bay Basin, Chefswet Basin, Isle Royale Basin, Marathon Basin, Keweenaw Basin Trough, Caribou Basin, Lake Superior Troughs, Wawa Trough, Batchwana Bay, Goulais Bay, and Whitefish Bay. Cores were taken 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. 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. Three additional 5.1 cm diameter sediment cores were obtained from L'Anse Bay, two from Chequamenon Bay, and twenty from the Keweenaw Peninsula region during 1996-7, using a KB Wildco gravity corer with plastic liners.

Cores were analyzed for copper, silver, and mercury following methods detailed in Kerfoot et al. 1999 and Rossmann 1999. The NOAA samples were analyzed at the EPA Grosse Ile lab for copper and silver by flame atomic absorption spectrophotometry (Perkin-Elmer model 5000). Analysis for total mercury utilized the cold vapor technique with a Perkin-Elmer AA and a Perkin-Elmer MHS-20 mercury/hydride system. Based on the standard deviation of blanks, the detection limit was 5 ng g^{-1} for 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) was analyzed to check metal extraction efficiency. Hg recovery (N=20) was 96.7±9.01%. The certified concentration for mercury in SRM 2704 was 1.47 µg g^{-1}.

Core Results. Background mercury concentrations at open Lake Superior sites ranged between 16-48 ng g^{-1}(mean±95%CL= 30.2±2.8 ng g^{-1}; CV= 25.5%, N=31), whereas concentrations in surface sediments varied between 27-957 (183.4±64.8 ng g^{-1}; CV= 98.3%). High copper and mercury were found near many mining locations. Anomalous high surface concentrations of mercury occurred south of Wawa (957 ng g^{-1}), in Thunder Bay (671 ng g^{-1}), and south of Thunder Bay (340 ng g^{-1}). The maximum mercury concentration in sub-surface sediments (2-20 cm deep) was 6,460 ng g^{-1}. Background total mercury fluxes to the lake varied between 0.20-0.72 ng cm^{-2} yr^{-1} (0.48±0.08 ng cm^{-2} yr^{-1}, CV=39.6%). Compensating for focusing factors produced total fluxes to surface sediments that ranged between 0.1-10.0 ng cm^{-2} yr^{-1} (3.2±0.5 ng cm^{-2} yr^{-}; CV=34.4%), whereas FF-corrected anthropogenic mercury fluxes to surface sediments varied between 0.7-10.0 ng cm^{-2} yr^{-1} (2.7±0.5 ng cm^{-2} yr^{-1}; CV=40.7%).

Around the Keweenaw Peninsula, background mercury concentrations averaged 40±10.3 ng g^{-1} , whereas surface mercury concentrations were higher than open Lake Superior values, ranging between 96.3-512.2 ng g^{-1} (mean 312.9±66.2 ng g^{-1}; CV= 42.7%, N=18). All cores had a buried peak (Fig. 1). Highest peak concentrations were recorded at Hancock (1780.6 ng g^{-1}), near Dollar Bay (1059.8 ng g^{-1}), and in Portage Lake (1009.6 ng g^{-1}). Peak mercury concentrations were highest near or downwind from smelter locations. Surface fluxes for mercury in the Keweenaw region ranged from 2.1-41.1 ng cm^{-2} yr^{-1}(mean 10.9±6.9 ng cm^{-2} yr^{-1}; CV= 113%; N= 14). All cores showed mercury fluxes rising initially with copper mining activity, and declining recently, after the close of stamp sand and smelting activities. Hg flux consistently peaked between 1900-1920, during the maximum period of copper processing and local smelter activity (Kerfoot et al. 1994, 1999).

Anthropogenic copper, silver, and mercury inventories were highly correlated (Fig. 2). Mercury inventories ranged from 297.5 ng cm^{-2} to 8432 ng cm^{-2}, with the anthropogenic fraction varying from 57.8% to 94.6%. The high correlation between silver and the other two metal inventories suggest geological ("rock") sources, since silver is not cycled through the atmosphere. Given the most recent estimate of sediment depositional area (68.5%), the surface 20 centimeters of sediment in Lake Superior contain an estimated 342 metric tons of mercury, of which 51% or 174 metric tons is anthropogenic. Twenty-nine metric tons of mercury are stored (ca. 1.9 metric tons yr^{-1}) within the surficial 2 cm of sediment [ca. 15 yrs), more than doubling the IJC estimate of loading (Rossman 1999). Of this, 22 metric tons or 74% is anthropogenic. By comparison, an estimated total of 8.4 metric tons of anthropogenic mercury are stored in Keweenaw Waterway sediments alone.

Does mercury occur naturally in copper and silver deposits? "Poor rock" ore samples obtained from five abandoned Peninsula mines were analyzed for copper, mercury, and silver. The rock samples were sieved into size fractions. Copper was present in all poor rock samples at relatively high values, ranging from 151-6,457 µg g^{-1} (mean±95%CL= 2,294.7±599.1 µg g^{-1}; CV= 73.8%; N=32). Silver was also present, ranging from 0.3-7.0 µg g^{-1} (2.40±0.62; CV= 72.6%; N= 32), close to the 1,000:1 ratio considered typical for regional native copper ores. Mercury concentrations in crushed samples of the parent basalt rock were very low, ranging from 2.0 to 5.0 ng g^{-1}. However, all fractions of the "poor rock" ore samples contained mercury, varying from 9-281 ng g^{-1} (85.4±24.7 ng g^{-1}; CV= 81.9%; N= 32).

Samples of stamp sands from ten mill sites also were analyzed for copper, silver and mercury. Again, copper concentrations in stamp sands were high, ranging from 366-16,163 µg g^{-1} (mean 4363.7±899.9; CV= 85.0%; N= 68). Also, samples sieved into size fractions demonstrated that copper concentrations were inversely related to grain size ($r = 0.387$, $p<0.01$, N = 41). Silver ranged between 0.6-8.7 µg g^{-1} (mean 3.15±0.52 µg g^{-1}; CV= 69.2%; N= 68), again close to the 1,000:1 ratio previously reported from ore deposits. Mercury was present in all stamp sand samples, ranging between 2.8-265 ng g^{-1} (mean 48.3±11.8 ng g^{-1} ; CV= 100.5%; N= 68). There was a significant inverse relationship between grain size and concentration ($r = 0.541$, $p<0.0005$, N=43), important because the finest size fractions are more likely to be transported further from shoreline stamp sand piles by wave action. For example, the readily dispersed “slime clay” fraction averages between 100-200 ng g^{-1} mercury. Multiplying the mean concentration of mercury by the amount of stamp sand discharged suggests that 12 metric tons of mercury were discharged by native copper mill operations alone into the Keweenaw Waterway (Harting 1999).

Samples of native copper and silver ores from seventeen abandoned peninsula mines were analyzed for copper, mercury, and silver (Table 1). All samples tested were found to contain mercury in relatively high concentrations. Mercury concentrations in native copper ores ranged between 0.9-19 µg g^{-1}, with means for different mines ranging between 1.1-9.4 (grand mean = 4.77±3.99 µg g^{-1}). Native silver ores from the Adventure Mine near Mass City contained on average ten times more mercury, ranging from 91.6 µg g^{-1} to 149.6 (mean 105.9 ± 38.6) µg g^{-1}, suggesting that silver ores contain more mercury than copper ores.

Mercury’s association with the copper, copper-silver, and silver metal mixtures, suggests that it occurs as a natural amalgam. Large amounts of metal ore were smelted at sites along the Keweenaw Waterway and Torch Lake. Multiplying the mean mercury concentration times the amount of metal processed gives an estimate of 38.9 metric tons released during smelting (Harting 1999; Kerfoot et al. submitted). This relatively large total explains why high mercury inventories are traceable back to smelter sites. In all, approximately 58.6 metric tons of mercury (smelting + stamp sands) were discharged from Peninsula mining operations alone, not including leaching from “poor rock” piles or imported amalgam mercury used in regional silver or gold mining operations (Nriagu 1994; Kerfoot and Nriagu 1999; Kerfoot et al. 1999).

We discovered that the Keweenaw Peninsula ore composition is not unique. Mercury occurs commonly in massive metal ore deposits as a trace contaminant. Assays on voucher specimens from Greenstone Formation ores in Ontario verify a widespread incidence of trace mercury (Kerfoot and Nriagu 1999; Kerfoot et al, submitted). High mercury concentrations are also characteristic of copper, silver, lead, and gold ores worldwide (Table 2). Mercury concentrations are high in massive gold-silver-copper ore deposits, but much lower in placer gold deposits. Whereas the Keweenaw Peninsula mercury is found predominately as a natural amalgam in native copper and silver metal ores, mercury is also found with a variety of massive ore minerals. These samples suggest a previously unrecognized, global incidence of mercury in metal ore deposits.

Evidence for mineral-bound mercury occurrence is scattered throughout the geological literature, often in hard-to-reach places. On the Keweenaw Peninsula, Luppens (1970) examined 315 core samples from 13 drill holes through the White Pine copper deposit of the Nonesuch Shale. Mercury was found throughout the deposit, ranging between 10-60 ng g^{-1}. Unfortunately, metal ores were not examined directly, as the research focussed on describing a “primary halo of mercury” just above and parallel to a Cu-Fe fringe deposit. On Silver Isle, Thunder Bay, Ontario, Wilson (1986) noted mercury as a naturally occurring amalgam (“Arquerite”, or mercurian silver, $Ag_{12}Hg$) in silver ore. Recently Cannon and Woodruff (1999) confirmed our earlier findings (Harting et al. 1996; Kerfoot et al. 1999; Harting 1999). Tailing deposits from copper mining on Isle Royale contained up to 14 µg g^{-1} Hg, similar to our reported high from the Keweenaw Peninsula. Again, the basalt bedrock had very low values (<5 ng g-1). The results on Isle Royale outcrops are important, for the strata are connected to Keweenaw Peninsula beds though a syncline relationship, independently verifying mercury in Portage Volcanic Series ore bodies.

Our survey of Lake Superior Basin mineral deposits suggests general incidence of mercury in copper, silver, and gold ores of the U.S. and Canadian Greenstone Belt deposits (Harting et al. 1996; Harting 1999; Kerfoot et al. 1999; Kerfoot et al., submitted). Concentrations are highest in silver ores, lower in copper and gold, but present in all tested samples. Ores from all over North America and the world contain mercury, suggesting widespread, perhaps global incidence. Processing of ores through smelting and leaching will likely release mercury to soils and the atmosphere, contributing to other recognized sources (Nriagu 1989; Kerfoot and Nriagu 1999). Sanberg et al. (1984) and Simpson et al. (1986) reported mercury in five gold ore loads, with concentrations that ranged between 3-31 µg g^{-1}. Moreover, they state that “gold and silver ores typically contain other metals such as mercury and a variety of base metals”, and express concern that mercury concentrated during modern-day cyanide solution processing could produce a health hazard during smelting or heap leaching. An additional watershed concern is that release of mercury through smelting, commercial leaching, or past amalgamation processing, could interact with ubiquitous wetlands or organic-rich sediments (Matty and Long 1995; Long et al. 1995; Kolak et al. 1999). Proximity of methylating environments, such as wetlands, is an immediate concern in the Lake Superior watershed, since these environments are often a source of methyl mercury (Hurley et al. 1999).

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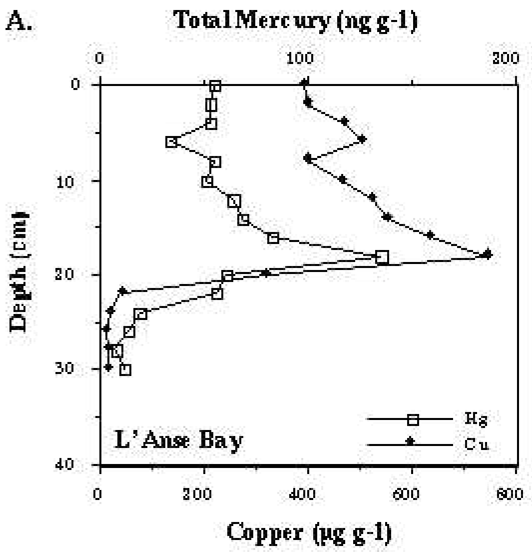

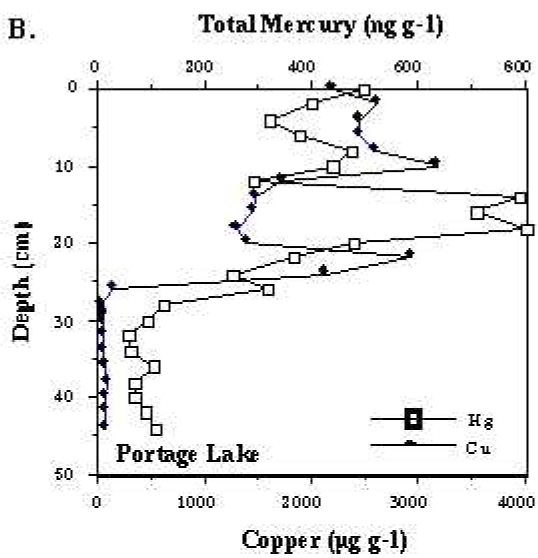

Fig. 1. Copper and mercury profiles for the Keweenaw Waterway (Portage Lake) and L'Anse Bay, Lake Superior. Note change in scales for the two elements.

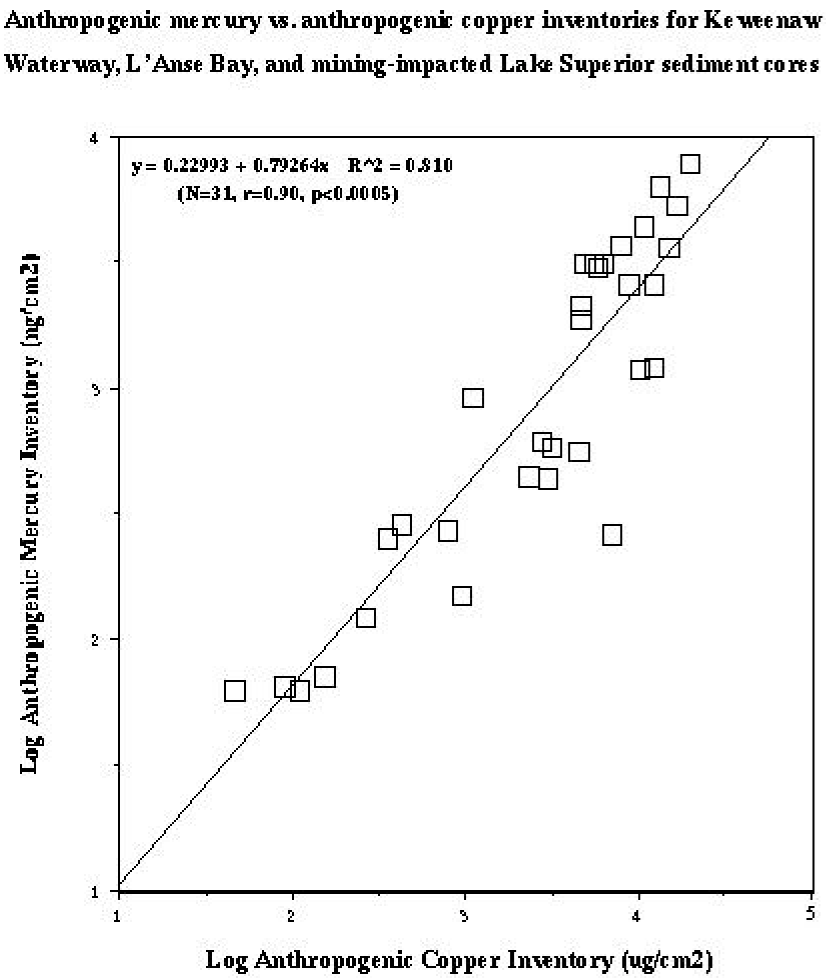

Fig. 2. High correlation between anthropogenic copper and mercury inventories for Keweenaw Peninsula region sediment cores.

Table 1. Mercury concentrations in copper, silver, and gold ores. For native copper and silver ores, % mass of copper listed. Standard deviations given in parenthesis after mean values.

Ore Source	**N**	**Copper % by mass**	**Mercury µg g-1**
Regional Copper Mines (Keweenaw Peninsula)			
Adventure	2.0	93.8 (0.7)	6.89 (4.58)
Archadian	2.0	84.0 (4.8)	2.99 (1.73)
Baltic	2.0	93.5 (8.3)	9.35 (2.12)
Caledonia	2.0	90.5 (0.7)	3.39 (0.35)
Centennial	2.0	75.1 (16.6)	2.70 (2.58)
Central	2.0	80.2 (0.6)	5.70 (5.26)
Champion	2.0	87.1 (2.2)	4.73 (1.88)
Cliff	2.0	87.9 (17.1)	6.54 (2.84)
Copper Falls	2.0	95.5 (6.3)	1.36 (0.11)
Globe	2.0	100.0 (0.0)	1.12 (0.18)
Hecla	2.0	50.7 (35.0)	5.64 (1.05)
Isle Royale	7.0	71.8 (15.4)	4.76 (4.99)
Quincy	2.0	95.2 (6.8)	7.10 (6.16)
Tamarack	2.0	80.0 (14.4)	5.60 (1.34)
Trimountain	2.0	67.6 (1.1)	5.73 (7.02)
White Pine	2.0	50.0 (11.4)	3.03 (0.39)
Silver			
Adventure (Silver Mine)	3.0	0.28 (0.23)	105.87 (38.61)
Cliff (silver half of half-breed)	1.0		981.3
Quincy (Copper Mine)	1.0	21.0	56.3
Half-breed (unknown source)	1.0	12.9	45.9

Table 2. Mercury concentrations in copper, silver, and gold ores. For native copper and silver ores'% mass of copper listed. Standard deviations given in parenthesis after mean values.

Mine Source	N	Mercury µg g-1	
Copper Ores			
Cadia Mine, New Zealand	2	2.22	(2.19)
Cerro del Passo, Peru	2	7.42	(9.02)
Dyer Mine (chalcocite), Utah	1	0.66	
Prospect Hill Mine (conglomerae Cu), Utah	1	0.25	
Ray, Arizona	2	2.83	(0.54)
San Bartolo (Cu in sandstone), Chile	1	0.72	
Silver Ores			
Beaver Mine (quartz, argentiferous galena), Ontario	4	1.29	(1.31)
Barre Frontense Co. (argentiferous galena), Ontario	1	1.81	
Dead Medium Mine (argentiferous galena), Washington1	1	34.94	
Kells Mines (native Ag, calcopyrite), Ontario	1	6.74	
Little Annie (argentiferous galena)	1	9.88	
O'Brien Mine, Ontario	1	7.16	
Oriole Mine (argentiferous galena)	1	1.85	
Lepha Lake claims (native Ag, diabase), Ontario	1	3.91	
Millaret Mine (galena), Ontario	1	12.51	
Silver Mt, Ontario	1	16.96	
San Bartolo (argentite)	1	244.30	
Uintah (Ag/Au ore), Utah	1	23.69	
White Silver Co. (smalltite/erythrite), Ontario	1	0.95	
Wildcat Mine, Washington	1	1.85	
Gold			
Belmore Mine, Ontario	1	11.07	
Buffalo Mine (ankerite), Ontario	1	0.22	
Carlin Mine, Nevada	1	15-17	(Simpson et al. 1968)
Cochenour-Williams Mine (arsenopyrite), Ontario	1	7.78	
Constock Mine (Au/Ag ore), Washington	1	12.08	
Cortez, Nevada	1	8-10	(Simpson et al. 1968)
Granite King Mine (Au/Ag/Cu ore)	1	7.36	
Getty Mine, Nevada	1	27-29	(Simpson et al. 1968)
Grass Valley (Au ore)	1	44.99	
Hollinger Mine, Timmons, Ontario	1	6.01	
Kerr-Addison Mine (auriferous quartz), Ontario	1	0.32	
Loclash Mine (covellite), Ontario	1	33.16	
Lorain Mining Co. (Au/Ag/Cu ore), Washington	1	39.61	
Mabec Mine (pelcite/Au quartz)	1	110.40	
McIntyre Mine (quartz, pyrite, sericite), Ontario	3	0.68	(0.19)
McLaughlin Mine (Au ore)	3	10.26	(8.31)
Missing Luck Claim, British Columbia	1	1.56	
Moltke Mine (auriferous pyrite)	1	0.94	
Ophir Mine, Ontario	1	0.70	
Oro Belle Mine	4	6.83	(6.65)
5-More, Nevada	1	3.00	(Simpson et al. 1968)
Pinson, Nevada	1	17.00	(Sandberg et al. 1984)
Tyree Mine (Au/Cu ore), Washington	1	17.64	
Verna Mine (Au/Ag ore)	1	30.07	
Washington Mine (Au/Ag/Cu ore)	1	3.45	