Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr



# Legacy mercury releases during copper mining near Lake Superior



W. Charles Kerfoot <sup>a,\*</sup>, Noel R. Urban <sup>b</sup>, Cory P. McDonald <sup>b</sup>, Ronald Rossmann <sup>c</sup>, Huanxin Zhang <sup>d</sup>

<sup>a</sup> Department of Biological Sciences and Great Lakes Research Center, Michigan Technological University, Houghton, MI 49931, USA

<sup>b</sup> Department of Civil & Environmental Engineering and Great Lakes Research Center, Michigan Technological University, Houghton, MI 49931, USA

<sup>c</sup> U.S. EPA, Mid-Continent Ecology Division, Large Lakes Research Station, Grosse Ile, MI 48138, USA

<sup>d</sup> Department of Geological & Mining Engineering & Sciences, Michigan Technological University, Houghton, MI 49931, USA

## ARTICLE INFO

Article history: Received 29 April 2015 Accepted 6 October 2015 Available online 21 November 2015

Communicated by Erik Christensen

Index words: Copper mining Sediment cores Mercury flux Methylmercury Keweenaw Peninsula Lake Superior

# ABSTRACT

To examine issues of mercury contamination in lake sediments and fish, we require insight into historic sources of mercury and details of watershed methyl mercury (MeHg) cycling. Modern-day National Atmospheric Deposition Program (NADP) estimates of atmospheric mercury deposition in the upper Midwest region range from  $4-10 \ \mu g/m^2/y$  (wet only) to  $5-30 \ \mu g/m^2/y$  (gross deposition). Sedimentary records from scattered Michigan lakes, removed from mining sites, record around  $5-24 \ \mu g/m^2/y$  modern THg deposition. However, these values are not representative of historic deposition near mining sites. On the Keweenaw Peninsula, mercury occurs naturally in copper ores and was discharged by smelting and stamp mill (tailings) operations. Here we examine mercury fluxes into two lakes (Portage and Torch Lake, portions of the Keweenaw Waterway) off Lake Superior, part of the previous Torch Lake Superfund site. Total mercury fluxes document greatly enhanced mercury loading (mean ca. 1590  $\mu g/m^2/y$ ; peaks of 5120 to 21,300  $\mu g/m^2/y$ ) during the height of copper mining (1880–1930), followed by a rapid decline once activities ceased. Methylmercury profiles appear to document both current methylation and historic methylation during mining operations. Time differences in MeHg and THg profiles may relate to watershed delivery time lags, toxic effects of copper on methylating bacteria, or to stratigraphic mobility. Whereas rapid sedimentation and lowered copper flux are promoting ecosystem recovery in Portage Lake, slower burial by organic-rich sediments is enhancing metal concentrations in Torch Lake sediments.

© 2015 International Association for Great Lakes Research. Published by Elsevier B.V. All rights reserved.

# Introduction

Contamination of the environment with mercury released from human activity is a global problem. In the U.S.A. alone, 30 statewide mercury advisories were issued for freshwater fish from lakes or rivers in 2010 (USEPA, 2010). All of the Laurentian Great Lakes except Ontario have fish advisories for mercury. The 2010 National Listing of Fish Advisories includes 4598 advisories covering approximately 7.16 million ha of lake area and 2.09 million km of river stretches, representing 42% of the nation's total lake area and 36% of the nation's total river network. Due to the scale of the problem, control of mercury emissions has become an urgent, yet contentious, issue. Four major medical and public health groups, as well as 13 states, are involved in lawsuits that claim that the U.S. government is not doing enough to protect people from mercury pollution.

Control of mercury concentrations in the environment requires knowledge of historic mercury sources and details of ecosystem cycling. To date, most attention has focused on atmospheric emissions of mercury. Due to large reductions in emissions from medical and municipal incinerators over the past 15 years, coal-burning power plants are now

\* Corresponding author. Tel.: + 1 906 487 2791.

E-mail address: wkerfoot@mtu.edu (W. Charles Kerfoot).

considered the single largest source of atmospheric mercury emissions in the U.S.A. (Cohen et al., 2004; Seigneur et al., 2004). Less successful have been attempts to quantify the magnitude of atmospheric emissions and tailings releases from metal ore mining sources. In the late 1990s into the 2000s, there was a curious discrepancy along U.S.–Canadian boundary waters (Kerfoot et al., 2004; Cooke et al., 2011). In Canada, the base metal mining and smelting industry was identified as the single largest source discharging mercury into the atmosphere, contributing 40% of total Canadian emissions in 1995 (Environment Canada, 2001). In 2000, the United Nations Environmental Programme (UNEP) and Environment Canada listed mining as the chief contributor of atmospheric Hg emissions in Canada, and the third most important contributor in the U.S., behind coal-burning electric power generation and incineration (Environment Canada, 2000; UNEP, 2002).

Before 1998, mining contributions were hardly recorded in the U.S. After 1998, when mining operations were first included in EPA's Toxics Release Inventory Program, mining operations were reported as the largest source of mercury emissions into the atmosphere in EPA region #9 (Nevada, Arizona, California; USEPA, 2003) and around Lake Superior (LSBP, 2002, 2011; Kerfoot et al., 2004). The metal industry is now considered the third largest contributor to recent U.S. atmospheric discharges (Cohen et al., 2011). Despite the closing of numerous mines, smelters, and a major sinter plant in the Lake Superior basin over the past 20 years, the Lake Superior Management Plan (LaMP) Commission still identifies mining as the single largest contributor of mercury in the Lake Superior watershed; a perspective restated by Dr. Susan Hedman, USEPA administrator, Region 5, at the Ashland, Wisconsin, Lake Superior Binational Forum meeting, March 23, 2012.

Yet the historic details of regional mercury loading from mining sources throughout the Lake Superior basin are poorly documented and researched. Production of monomethylmercury  $(CH_3Hg^+)$  associated with mining activities is well recognized worldwide (Lebel et al., 1998; Horvat et al., 2002), but varies greatly from site to site. The challenge is to measure point discharge estimates and to place these into a regional watershed context, clarifying pulses of release and attempting to measure the extent of spatial impacts on the ecosystem as mercury is cycled (Fisher et al., 2012). In addition to atmospheric emissions during smelting and concentrate purification, the mass of mercury remaining at some mine smelter and tailings sites is one to two orders of magnitude greater than that emitted into the atmosphere during ore processing (Wong et al., 1999; USEPA, 2003). Emissions of Hg<sub>(0)</sub> to the atmosphere from mercuric sulfide and gold mine wastes have been measured and were estimated to represent 99% of environmental releases in southwestern USA arid regions (Gustin et al., 2003; Nacht et al., 2004).

Methylated species of mercury can bioaccumulate through food chains to concentrations that are potentially dangerous for top-level consumers. In northern forested regions, juxtaposition of mining sites with wetlands, stream and river systems, and interconnected lakes could enhance contamination effects by elevating regional methylation rates. Historic acid-mine drainage was observed to release mercury to streams in California. This mercury was bioavailable, as indicated by a correlation between concentrations in macroinvertebrates and contaminated streambeds (Fischer and Gustin, 2002). Lake and river sediments in Nova Scotia were contaminated with mercury for some distance downstream of gold mines (Wong et al., 1999). Clearly, some of the mercury from mine activity is mobilized as  $CH_3Hg^+$  into the environment, yet key issues that remain to be resolved include identifying release points and loading amounts, quantifying rates of methylation, and determining watershed influences on subsequent storage and transport.

The Keweenaw Peninsula juts out into Lake Superior from the Upper Peninsula of Michigan (Fig. 1). The Keweenaw coastal and embayment sediments have much more copper, silver and mercury than can be



Fig. 1. Geographic position of the Keweenaw Waterway, showing coring sites. The Waterway (star) occurs midway up the Keweenaw Peninsula, a portion of the Upper Peninsula of Michigan that juts into Lake Superior. Large Xs indicate the three coring locations where we measured total and methyl Hg profiles. Solid circles mark other coring locations where Cu and total Hg fluxes were previously measured. Three additional coring sites along the narrow North Entry corridor west of Portage Lake are not shown. Dark coastal regions indicate above-water shoreline stamp sand piles, whereas shoreline hollow squares and circles indicate stamp mill and smelter sites.

explained on the basis of long-distance regional atmospheric deposition (Kerfoot et al., 2002, 2009; Gewurtz et al., 2008). Excess metal inventory in interior (Table 2; Fig. 2) and coastal sediments presumably reflects one or more of the following: 1) accelerated erosion of natural ore deposits that contain elevated metals (Kolak et al., 1999; Kerfoot et al., 2002), 2) discharges of mine wastes into rivers or along coastlines (Kerfoot et al., 1994, 2012; Jeong et al., 1999; Urban et al., 2004), and/ or 3) regional smelter activities that broadcast emissions broadly over watersheds (Kerfoot et al., 2004; Greenaway et al., 2012). Here we utilize dated sediment cores to examine metal (Cu, THg) loading chronologies in two nearby lakes (Portage and Torch Lakes) and test if ore-associated mercury is methylated during the copper-mining era.

On the Keweenaw Peninsula, there is an opportunity to gain historical insight due to the remote location (fewer conflicting sources), proximity to lakes, suitable lake sediments for coring, and surrounding wetland tracts. Results presented here quantify total mercury loading for over a century of mining activity, and reveal that methylation occurred at the time of mining operations and shortly afterwards, with an apparent time lag. Elevated concentrations of metals also persist at some sites decades after cessation of mining activities, creating "lingering effects".



**Fig. 2.** In Portage Lake cores, X-rays of sediment reveal a rich sequence of varve-like clay bands in mid-core strata that derived from annual copper mill discharges. The distinctive bands offered outstanding opportunities for accurately determining time horizons and fluxes from the beginning of mill operations (late 1850s) to mill cessation (1947). The dense bands correspond to slime clay fractions of tailings discharged under ice during winter.

# Methods & materials

#### Site description & background

Between 1850 and 1929, the Keweenaw district was the second largest producer of copper in the world and a key part of the early Industrial Revolution (Murdoch, 1943; Benedict, 1952). During that interval, 140 mines worked the central deposits of the Peninsula and over 40 mills processed ores. The concentration of copper in the parent rock averaged between 0.5 and 6.1% of total mass, as mills discharged vast amounts of tailings, the so-called "stamp sands", from giant steamdriven stamps (Benedict, 1955). In total, smelting of native copper deposits produced 4.8 million metric tons of copper (Bornhorst and Lankton, 2009). The Keweenaw Waterway (Fig. 1), part of the Torch Lake Area of Concern and previous Torch Lake Superfund site, was heavily impacted by copper mining between about 1860 and 1968 (USEPA, 2001). The Waterway bisects the Peninsula and includes Portage and Torch Lakes plus two channels that discharge into Lake Superior (North & South Entry). Both Portage and Torch Lakes were heavily impacted by large smelter and mill discharges (Fig. 1). Around the Keweenaw, the concentrations of several metals (e.g. copper, silver, zinc, mercury, chromium, cobalt) are highly correlated in mining era sediments, suggesting common rock sources. Neutron Activation Analysis was used to fingerprint the elemental composition of individual stamp mill ores and to reconstruct historic mill discharges into Portage Lake, confirming the mining sources of metals found in sediments (Kerfoot and Robbins, 1999; Kerfoot et al., 2002). However, the Neutron Activation Analysis did not include mercury.

In the Keweenaw Waterway, Portage Lake had eleven copper stamp mills (7 early gravity-driven stamp mills, 4 later large steam-driven mills) between 1855 and 1947, as well as four smelters along its shoreline (Kerfoot et al., 1994). Six large stamp mills and a smelter operated on the shores of Torch Lake between 1868 and 1968. Coarse "stamp sand" tailings were deposited in the immediate vicinity of stamp mills (Fig. 1; tailings piles), whereas the metal-rich "slime" (i.e., clay-sized) fraction of the tailings dispersed into the deeper regions of the lakes (Fig. 2, notice midcore bands). Of the two water bodies, Portage Lake was less environmentally impacted for several reasons: less discharged tailings, the larger lake and watershed drainage area, and the higher natural sedimentation rate (Table 1). A total of 34 million metric tons of copper tailings were sluiced into Portage Lake, whereas 179 million metric tons were discharged into Torch Lake (Kerfoot et al., 1994). Portage Lake is 4.6 times larger, shallower and polymictic compared to the stratified Torch Lake (Churchill and Kerfoot, 2007). The Portage Lake watershed has a much larger catchment area than Torch Lake (26 times larger) and receives more uncontaminated sediment runoff from several large rivers and streams, including the extensive Sturgeon River Sloughs and Pilgrim River drainage. Because of these inputs, post-mining sedimentation rates in Portage Lake are much higher (60–120 mg/cm<sup>2</sup>/y; Kerfoot and

#### Table 1

Key limnological features of Portage and Torch Lakes, Keweenaw Peninsula, Michigan. Sediment focusing factor estimates are from Kerfoot and Robbins (1999) and McDonald and Urban (2007). The wetland estimate for each lake is for the entire Keweenaw Waterway watershed.

Variable	Portage Lake	Torch Lake
Surface area (km <sup>2</sup> )	44.4	9.7
Maximum water depth (m)	16	37
Mean water depth (m)	9	15.2
Watershed area (km <sup>2</sup> )	5200	200
Stratification	Polymictic	Dimictic
Stamp sand discharged (Mt)	34	179
Year mill discharges ended	1947	1968
Modern sedimentation rate mg/cm <sup>2</sup> /y	60-120	20-30
Focusing factor	1.3-1.7	0.2-1.7
%Wetlands (Keweenaw Waterway)	10.5	10.5

Robbins, 1999) than in Torch Lake (20–30 mg/cm<sup>2</sup>/y; McDonald and Urban, 2007; McDonald et al., 2010).

In addition to larger amounts of tailings discharged into waters, Torch Lake is relatively deep (37 m max. depth, 15.2 m mean depth) and has a water residence time of about 1 year (Warburton, 1987). A single large tributary, the Trap Rock River, provides 60% of river inflows. The lake is dimictic, with summer stratification, a well oxygenated hypolimnion, and a modern summertime Secchi depth of 3.5 m. Water from Torch Lake flows into the more extensive Portage Lake. When the last mill on Torch Lake closed in 1968, 20% of the original lake volume was filled with mine spoils, i.e. shoreline stamp sand piles and offshore "slime clays" (Fig. 1; USEPA, 2001). Torch Lake was put on the National Priority List in 1986, but the lake itself was left to recover on its own, whereas the exposed stamp sand piles on the shores were covered with top soil and revegetated between 1999 and 2004 (Torch Lake Superfund Program). Dissolved copper concentrations in lake water dropped from a high of  $25-100 \,\mu\text{g/L}$  (ppb) in the 1970s to 14-23  $\mu\text{g/L}$  in the 1990s as a result of recovery (Diaz, 1973; Lytle, 1999; USEPA, 2001).

# Regional copper & silver ore analysis

To identify the primary source of mercury associated with Keweenaw mining, ore samples were collected from several mine sites. Subsamples were digested in a Milestone ETHOS 900 microwave digester, and analyzed for total mercury by the cold vapor technique using a Perkin-Elmer Model 5000 and a Perkin-Elmer MHS-10 mercury-hydride system at Michigan Technological University (MTU). For every set of 10 samples, a minimum of two sets of standards were analyzed, in addition to two procedural blanks and one duplicate sample. Natural matrix certified reference materials included: Metals of soil/sediment #4 (Ultra Scientific; SRM 2704a) and Buffalo River sediment (National Bureau of Standards, NIST 1990). Mercury recovery from these reference materials was 96.7  $\pm$  9.0% (n = 35). To ensure quality control and quality assurance (QC/QA), selected ore sample extracts (5% total) were split and analyzed independently at the Grosse Ile, Michigan USEPA Lab. There was 90.4% (range 73.0 to 98.6%) agreement between results of the Grosse Ile Lab and MTU analyses.

## Sediment sampling and analyses

Sediment cores were collected with a 5-cm diameter K-B style gravity corer (WildCo). Multiple cores were collected at two sites (10- and 20-m water depths) for extended analysis (Cu, THg, and MeHg) in the eastern half of Torch Lake and two cores were collected at a single site (14-m water depth) in Portage Lake (Fig. 1, x-sites, "MeHg cores"). Another set of 12 cores previously collected only examined THg and Cu fluxes ("THg cores", solid circles, Fig. 1; see Kerfoot et al., 2004). Cores of 60–80 cm length were retrieved at all sites, brought to the lab and X-rayed at Portage Health Hospital to aid in the correlation of depths and ages (Fig. 2). Sediments were then extruded and sliced into 1-cm depth increments. For the "MeHg cores", a portion of the core slices was dried and ground, and then analyzed for <sup>210</sup>Pb (Fig. 3) and copper. Another portion of the slices was preserved wet and shipped on dry ice to the USEPA Lab at Grosse lle for measurement of mercury species.

Analyses for <sup>210</sup>Pb (sediment dating) and Cu were done at MTU. Total <sup>210</sup>Pb was measured (as the daughter isotope, <sup>210</sup>Po) by alpha spectrometry (EG&Ortec Octete Plus) following extraction and plating by the methods of Eakins and Morrison (1978) as modified by Engstrom et al. (1985). Isotope extraction and plating efficiencies were measured by spiking all samples with known activities of <sup>209</sup>Po. Supported <sup>210</sup>Pb and <sup>137</sup>Cs were measured on all samples by gamma spectrometry (low background Germanium well detectors, Ortec DSpec model spectrometer); supported <sup>210</sup>Pb was calculated as the average of eight <sup>214</sup>Bi and seven <sup>214</sup>Pb peaks. Profiles in Portage and Torch Lake showed continuous, uninterrupted deposition (Fig. 3). Dating of the Portage Lake core was preceded by extensive <sup>210</sup>Pb, <sup>137</sup>Cs, and varve dating studies at additional sites (Fig. 1; 12 "THg sites", Kerfoot and Robbins, 1999; Kerfoot et al., 2004).

The <sup>210</sup>Pb profile in Torch Lake sediments and its interpretation are complicated somewhat by (1) the drastic change in sedimentation rate associated with cessation of mining, and (2) the very high activity of supported <sup>210</sup>Pb in the mining residues. Dating of the full profiles is discussed elsewhere (McDonald, 2005; McDonald and Urban, 2007). At both sites, the <sup>210</sup>Pb profiles appear to fit the CIC-CRS model (Robbins, 1978) as evidenced by a log-linear decrease in <sup>210</sup>Pb activity with mass depth (Fig. 3). However, an even better fit to Torch Lake profiles was obtained with a slightly modified CRS model (Fig. 3 right 3 panels; McDonald and Urban, 2007). The standard CIC-CRS model underestimates the sedimentation rate and overestimates the age of the sediments. As explained in McDonald (2005) and McDonald and Urban (2007), a modified CRS model (Appleby and Oldfield, 1978) was developed that provides more precise agreement with <sup>137</sup>Cs peaks (not shown here) and mining history.

Sediments were digested in the microwave (CEM MDS-2100) using EPA method 3051A prior to measurement of total copper. Copper was measured using a Perkin-Elmer model 3100 spectrophotometer. Digestion efficiencies were verified using NIST standard reference material Buffalo River Sediments (SRM 2704), and instrument calibration was



Fig. 3. <sup>210</sup>Pb geochronology of recent sediments (14-m water depth site in Portage Lake, 20-m site in Torch Lake): a) excess <sup>210</sup>Pb profile from the central site in Portage Lake; b) excess <sup>210</sup>Pb profile from the 20-m Torch Lake site. The small rectangle in the upper left panel of Torch Lake strata is expanded to fill the two right panels, illustrating the log regression fit to <sup>210</sup>Pb values and the modified CRS model.

checked using the Plasma-Pure standard from Leeman Labs, Inc. Digestion efficiencies averaged 104%, and the calibration standard was, on average, measured as 101% of the certified value.

As mentioned earlier, mercury analysis was done at the USEPA Grosse lle Lab. Wet sediment samples for mercury analyses were subsampled. Those for total mercury analysis were freeze-dried and stored dry, whereas those for methyl mercury were weighed into pre-weighed vials and stored frozen. Water contents determined at the time of freeze-drying were used to convert methyl mercury wet weight results to dry weight results. Total mercury was analyzed by using a LECO AMA-254 mercury analyzer (LECO, 2003). Within the instrument, dry samples were thermally combusted to release mercury. All mercury was converted to Hg<sup>0</sup> within a catalyst chamber. The Hg<sup>0</sup> was collected on a gold trap. After collection, the gold trap was heated, releasing the mercury for detection with an atomic absorption spectrophotometer.

Methyl mercury was analyzed using a PS Analytical Hg 7000 mercury speciation system. Major components of the system are an Agilent 6890 GC system and a PSA 10.750 detector. The method used was a slight modification of the Cai et al. (1997) method which was based on the original work by Jones et al. (1995). Using this method, samples were extracted with acidic potassium bromide/copper sulfate solution. The brominated mercury species were dissolved into methylene chloride for separation. The mercury species were then back extracted into sodium thiosulfate solution, extracted with acidic potassium bromide/copper sulfate solution, and dissolved into methylene chloride. After passing through an anhydrous sodium sulfate column, the methylene chloride to the gas chromatograph to separate the various species. As each species was driven off the column, it was converted to Hg<sup>0</sup> in a pyrolyzer and was quantified with an atomic fluorescence detector.

#### Results

## Background regional mercury fluxes

Before discussing long-term trends in sediment cores, regional atmospheric deposition records provide valuable modern-day Hg flux comparisons (Figs. 4a, b). Due to intense monitoring activities over the past decade, much is now known about recent atmospheric deposition of mercury in the Lake Superior Basin due to efforts of the National Atmospheric Deposition Program (NADP). The estimated rate of regional atmospheric wet deposition of total mercury in the upper Midwest (THg) ranges between 4 and 10  $\mu$ g/m<sup>2</sup>/y (Seigneur et al., 2004; Cohen et al., 2004) and is fairly uniform across the Upper Peninsula of Michigan, Wisconsin, and northern Minnesota (Fig. 4a; Table 2). For example, five-year (2004–2008) THg wet deposition at the nearby Mercury Deposition Network (MDN) site in Florence, WI, averages 6.6  $\mu$ g/m<sup>2</sup>/y. Today, Upper Peninsula wet deposition values contrast with higher rates downstate, near industrial regions (10.1–12.0  $\mu$ g/m<sup>2</sup>/y, Risch et al., 2011). For example, over a 10-year period (1994–2003), THg wet deposition was 2.1 times greater in the Lower Peninsula of Michigan (Dexter, MI, near Detroit) than at the Eagle Harbor monitoring station in the Keweenaw Peninsula (Keeler and Dvonch, 2005; Risch et al., 2011). Gross atmospheric deposition (wet + dry) in the region is harder to estimate, although recent measurement and modeling attempts suggest ranges for gross deposition between 5 and 30  $\mu$ g/m<sup>2</sup>/y (Fig. 4b; Zhang et al., 2012).

Estimates of THg fluxes from small isolated regional lake sediments (Table 2) range near or slightly higher than the 5–30  $\mu$ g/m<sup>2</sup>/y gross deposition range, varying between 15 and 95  $\mu$ g/m<sup>2</sup>/y in Minnesota (Engstrom et al., 2007), 5–9  $\mu$ g/m<sup>2</sup>/y in Wisconsin (Watras et al., 1994), and 2–24  $\mu$ g/m<sup>2</sup>/y in the Upper Peninsula of Michigan (Kerfoot et al., 2002). However, these values come from isolated lakes, removed from the immediate neighborhood of mining sites. Lake sediment values also reflect watershed loading and, unless corrected, sediment focusing. Sediment focusing within a lake, i.e. redeposition from margins into deeper regions, will elevate observed fluxes, e.g. a sediment focusing factor of 2.0 will double mean deposition network values. Published deep-water fluxes from Lake Superior (Rossmann, 1999; Rolfhus et al., 2003; Gewurtz et al., 2008), are usually relatively low  $(27-32 \,\mu\text{g/m}^2/\text{y})$ , especially if corrected for sediment focusing. Off the Keweenaw Peninsula (metal "halo" region) metal values begin to increase, especially along tailings-contaminated shorelines (Kerfoot et al., 2012). In the Keweenaw Waterway, surface fluxes for THg achieve levels several-fold above NADP and small isolated lake values (Table 2; mean, 109  $\mu g/m^2/y$ ).

## Mercury source in Keweenaw ores

In the Keweenaw, the primary historical regional source of mercury is from mining. When samples of native copper and silver from 29 abandoned Keweenaw mines were analyzed for mercury (Table 3), all contained trace mercury at relatively high concentrations ( $\mu$ g/g; also see Kerfoot et al., 2004, 2009). The metal Hg concentrations ranged between 83 and 6570 times the lithospheric average of 0.06 ppm



Fig. 4. Atmospheric mercury deposition across the states of Minnesota, Wisconsin, and Michigan, color contoured: a) left panel, wet deposition compiled from National Atmospheric Deposition Program (NADP), showing position of, and median values for, monitoring sites (after Gay, 2009); b) modeled estimates of gross deposition in the Great Lakes region, reconstructed following Zhang et al. (2012).

## Table 2

Comparing total mercury (THg) surface fluxes  $(\mu g/m^2/y)$  estimated at regional Atmospheric Mercury Deposition Network (MDN) sites with sediment values estimated from various lake locations (\* indicates focusing corrected, 137-Cesium).

Location	Ν	Range	Mean $\pm$ 95% C.L.	Source
Atmospheric NADP:				
Lake Superior Basin	8	4-5	$4.9\pm0.5$	Gay (2009)
Lake Superior Region	6	6-8	$6.6\pm0.5$	Butler et al. (2007)
Lake Sediments:				
Wisconsin Lakes	7	5-9	$6.7\pm0.5$	Watras et al. (1994)
WUP Lakes	16	5-24	$11 \pm 4$	Kerfoot et al. (2002)
("undisturbed")				
N. Minnesota Lakes	16	15-95	$39\pm23$	Engstrom et al. (2007)
Lake Superior	6	1-70	$27\pm26$	Kemp et al., 1978
Lake Superior	20	1-100	$32 \pm 11$	Rossmann (1999)
Lake Superior,	19	8-100	$39\pm14^*$	Kerfoot et al. (2004)
Keweenaw "halo"				
Lake Superior,	19	10-360	$73 \pm 48$	Kerfoot et al. (2004)
Keweenaw "halo"				
Keweenaw Waterway	14	21-411	$109\pm69$	Kerfoot et al. (2004)

(Wedepohl, 1995). Mercury concentrations in native copper varied between 0.1 and 47.1 µg/g, with a mean of  $3.9 \pm 2.1$  µg/g or ppm (mean  $\pm$  SD; N = 60). The relatively high concentrations in "native copper" seem facilitated by the presence of silver, found in "Lakes Copper" at a ratio of 1:1000. The association is evident in Cu–Ag mixtures, as the higher the concentration of silver, the higher the concentration of mercury

#### Table 3

Mercury concentrations in copper and silver ores from Keweenaw Peninsula copper mines. Concentrations in  $\mu g/g$  (ppm). Voucher numbers are available from the Seaman Mineral Museum, Michigan Tech, Houghton, Michigan. Standard deviations are given in parentheses after mean values.

Mines	Locations	Ν	Mercury (µg/g; mean, SD)				
A. Copper mines (native copper assays)							
Adventure	Mass	2	6.9 (4.6)				
Archadian	Hancock	2	3.0 (1.7)				
Baltic	Baltic	2	9.4 (2.1)				
Caledonia	Mass City	3	2.5 (1.6)				
Centennial	Calumet	2	2.7 (2.6)				
Central	Central	4	6.5 (1.1)				
Champion	Painesdale	7	3.3 (2.2)				
Cliff	Phoenix	5	5.5 (3.4)				
Copper Falls	Central	4	1.3 (0.2)				
Globe	Painesdale	2	1.1 (0.2)				
Hecla	Calumet	5	4.3 (3.6)				
Isle Royale	Houghton	5	1.9 (0.8)				
Lake Mine	Lake Mine	3	3.1 (1.3)				
Mass	Mass City	3	2.7 (0.6)				
National Mine	Rockland	6	3.0 (1.4)				
Northwest	Central	3	0.5 (0.3)				
Phoenix	Phoenix	3	2.3 (0.6)				
Quincy	Hancock	2	7.1 (6.2)				
Tamarack	Calumet	2	5.6 (1.3)				
Trimountain	Trimountain	2	5.7 (7.0)				
White Pine	White Pine	5	2.4 (1.1)				
B. Half breeds (cop	per & silver mixture)						
Unnamed	Keweenaw Peninsula	1	45.9				
Ojibway	Mohawk	2	0.9 (0.3)				
Phoenix	Phoenix	2	230.1 (237.2)				
Quincy	Hancock	1	38				
St Clair	Phoenix	3	2.8 (1.9)				
White Pine	White Pine	1	7.7				
C. Silver							
Adventure	Mass City	3	10.9 (38.6)				
Caledonia	Mass City	2	408.5 (83.6)				
Calumet/Hecla	Calumet	5	459.2 (224.3)				
Central	Central	1	2548				
Kearsarge	Kearsarge	2	289.5 (112.6)				
Mohawk	Mohawk	2	80.6 (23.1)				
Quincy	Hancock	1	56.3				
White Pine	White Pine	3	330.4 (274.9)				

(Table 3). Concentrations of mercury in half-breeds (mixtures of copper and silver) are substantially higher than in copper ore, ranging between 0.7 and 981 µg/g (mean =  $154 \pm 198 \mu$ g/g; N = 10), whereas concentrations in native silver vary between 34 and 2548 µg/g (mean =  $394 \pm$  $187 \mu$ g/g; N = 30). Exceptionally high values are also found in the associated gangue zinc mineral sphalerite (mean =  $190 \pm 55 \mu$ g/g, N = 6). The essential point here is that Hg occurs naturally in native copper, native silver, and zinc mineral samples from the Keweenaw ore deposits, apparently as a solid solution substitution into the mineral lattice (Kerfoot et al., 2002; Cooke et al., 2011). Locally, mercury from ore was released during smelting emissions (an estimated 20–24 tons of THg) and tailings discharges (an estimated 17–18 tons of THg; Kerfoot et al., 2004, 2009).

## Portage Lake mercury and copper flux profiles

The Keweenaw Waterway was a heavily industrialized region during the mining era. From 1855 to 1947, 16 stamp mills discharged 34.3 million metric tons of tailings into Portage Lake, and four shoreline smelters processed concentrates for copper and silver (Kerfoot et al., 1994, 2004). In Portage Lake sediment cores, the mining era is marked by annual banding, yet the interval covers only a 18–28 cm span of the vertical profile (Fig. 2). The sequence is marked by metal-rich winter discharges that resemble varves in X-ray photographs. In Fig. 5, the mine strata correspond to regions of lower porosity. The varved sequence is interrupted by a 1-2 cm band of brown sediments deposited during the Great Depression, when milling ceased. This interval is followed immediately by a series of fine bands from the remaining mill discharges (Isle Royale Mine) during a brief resurgence of mining activity in World War 2 that lasted until 1947 (Kerfoot et al., 1994; Kerfoot and Robbins, 1999). The WW II strata are overlain by a 12–19 cm sequence of postmining organic-rich sediments (Figs. 2, 5). In Portage Lake, the brown, organic-rich post-mining sequence began to accumulate about 20 years earlier (1947) than in Torch Lake (1968) and is noticeably thicker. Sedimentation rates in Portage Lake near the coring site were previously documented to be in the range of 60–120 mg/cm<sup>2</sup>/y (Kerfoot et al., 1994; Kerfoot and Robbins, 1999). The average sediment accumulation rate for post-mining sediments in the core described here is  $59 \text{ mg/cm}^2/\text{y}$ ; in relatively good agreement with prior measurements.

We used <sup>210</sup>Pb profiles and varve counts (see Methods & materials) to date the strata and to calculate fluxes for copper (Cu) and total mercury (THg). In the Portage Lake core, measurements of flux help correct for dilution and concentration effects associated with variable sedimentation. Fluxes for copper and total mercury are historically correlated (N = 23, r = 0.844, p < 0.001), increase with discharges after 1868, and achieve major peaks during the middle of the mining era (Fig. 5). There are two peaks of 12,240 and 8130  $mg/m^2/y$  for Cu and two peaks of 7080 and 5120 µg/m<sup>2</sup>/y for THg. Thus during the mining era, mercury fluxes at this site were 240 to 1400-fold greater than the present day gross atmospheric deposition  $(5-30 \,\mu\text{g/m}^2/\text{y})$ . After cessation of mill operations in 1947, fluxes for both Cu and THg declined rapidly, but still remained elevated above background (THg, 21–411  $\mu$ g/m<sup>2</sup>/y). Thus the Portage Lake profiles confirm that mercury deposition was substantially elevated during native copper mining activity. Peak fluxes for both copper and mercury were attained between 1880 and 1930, the primary period of copper production.

Across Portage Lake, pre-mining THg concentrations were relatively low, but variable, averaging  $39 \pm 5$  ng/g (Kerfoot et al., 2004). Some site variation exists because the lake rests over ore deposits. At the core site analyzed here, pre-mining concentrations for THg ranged between 127 and 168 ng/g (ppb). Concentrations increased during mining in the strata, achieving the highest values (ca. 1000 ng/g) in organic-matter-rich lake sediments deposited during the Great Depression (Fig. 5). Concentrations were only moderately elevated (~300 ng/g) in mine strata deposited during WW II, but increased to a secondary peak (450 ng/g) in the organic-matter-rich sediments laid down immediately after WWII.



**Fig. 5.** Sediment profiles at 14-m (central) site in Portage Lake. Profiles include porosity, total copper concentration ( $\mu$ g g<sup>-1</sup>), total Hg and methyl mercury (both in ng g<sup>-1</sup>) concentrations, ratios of methyl to total Hg (%MHg), and net accumulation rates (fluxes) for Cu (mg/m<sup>2</sup>/y) and Hg ( $\mu$ g/m<sup>2</sup>/y). The horizontal lines demarcate dated historical periods. Major fluxes for Cu peak between 1868 and 1947 and correspond to tailings ('slime clay') discharges from stamp mills into the lake. Superimposed total Hg fluxes show a similar pattern, following build-up of local smelting capability (1880–1938). MeHg concentrations before mining are low, increase during mining (1868–1947), peak during the Depression (1930–1938) and immediately following mill closure (1947), then decline to low values at present.

Total mercury concentrations in sediments deposited after cessation of mining decreased from 400 to 250 ng/g. Although influenced by sediment dilution effects, metal concentrations are important historic indicators, as they correlate with toxicity effects on benthic organisms and are associated with mercury transfer up the food chain.

In Portage Lake sediments, methyl mercury (MeHg) was present throughout the mining era (Fig. 5). Although there are fluctuations, MeHg concentrations rise slowly throughout the mining era, reach peak concentrations during Depression-era sediments, show a post-WWII sub-peak, and then decline substantially in post-mining strata. The concentration of mercury present as methyl mercury generally varied between 1 and 3 mg/g MeHg (0.1–0.3% of THg). A regression of methyl mercury on total mercury was highly significant (Portage Lake; y = 0.002X - 0.203; r = 0.775; N = 44, d.f. = 1, F = 62.8, p = 7.11E - 10). The MeHg on THg regression slope was 0.00198 with a SE  $\pm$  0.00024, i.e. MeHg averaged about 2.0 mg/g or about 0.2% of THg (Fig. 5). Ratios of MeHg/THg in Portage Lake are in relatively good agreement with reported modern values from several sites, suggesting little decomposition loss, although they seem slightly on the low side. Elevated MeHg concentrations extend beyond the active mining era, appearing to exhibit a "time-lag". However, there are several potential explanations for the displaced pattern (watershed delivery, toxic effects of Cu on methylating bacteria, sediment core mobility) considered in the Discussion section.

Additional information on THg versus Cu fluxes comes from twelve core sites scattered about the Keweenaw Waterway (circles in Fig. 1;

#### Table 4

Regressions of THg on Cu flux through time at various sediment core sites from the Keweenaw Waterway (Fig. 1, labeled with solid circles; three additional sites are on North Entry corridor, west of Portage Lake). The two variables (THg flux,  $\mu g/m^2/y$ ; Cu flux,  $mg/m^2/y$ ) are significantly highly correlated (\*\*\*, p < 0.001) at all locations, although the relative rates (regression slopes) and peak THg values (concentration,  $\mu g/g$  or ppm) vary, depending on proximity to smelter or stamp mill sources.

Core site	N (cm slices)	R (correlation) Hg and Cu flux	Regression equation	Peak THg concentration	Peak THg flux
1 NLS	35	0.661***	y = 0.300X + 4.8	595	871
2 DH	49	0.827***	y = 0.512X + 1.0	1010	1328
3 CC	35	0.676***	y = 0.087X + 26.5	680	845
4 OB	31	0.701***	y = 0.080X + 4.5	130	139
5 PB	41	0.895***	y = 0.534X + 12.5	369	428
6 CG	39	0.610***	y = 0.565X + 16.1	1060	5027
7 DB-1	51	0.706***	y = 0.093X + 31.2	648	1276
8 HAN	29	0.709***	y = 0.748X - 4.4	1021	2315
9 IR	37	0.542***	y = 0.400X + 24.8	850	2701
10 SLS	39	0.607***	y = 0.363X + 16.4	853	2842
11 SP	37	0.695***	y = 0.269X + 10.4	776	1064
12 HB	39	0.594***	y = 0.500X + 3.8	118	197

Table 4; Kerfoot et al., 2004). Peak THg concentrations at these sites during the mining era range from 130 to 1060 ng/g (mean = 676 ng/g; SD = 325), and THg fluxes range from 139 to 5027  $\mu$ g/m<sup>2</sup>/y (mean = 1586  $\mu$ g/m<sup>2</sup>/y; SD = 1416). The Waterway values again emphasize elevated loading across the lake bottom during the mining era (i.e. 4–168 times present-day MDN values). Significant correlations are present between the two variables (THg, Cu fluxes) because of jointly elevated values during the mining era (Table 4; r = 0.542–0.895). However, the temporal patterns are not identical. Correlations are not perfect and regression slopes vary by site, probably because there were two different sources (smelters, stamp mills). The primary source of THg was smelter emissions, whereas the primary source of Cu was stamp mill discharge (Kerfoot et al., 2004).

# Torch Lake mercury and copper flux profiles

Torch Lake varies from Portage Lake in several important aspects: 1) a much greater amount of mine tailings discharged (Table 1; 5.2 times greater amount), 2) deposition into a smaller area (4.6 times smaller), 3) historical application of different extraction practices (mill discharge plus dredging of older tailings piles and subsequent chemical flotation treatment; Benedict, 1955), 4) a later date of cessation from discharges (ca. 20 years later, 1968 versus 1947), and 5) a lower rate of post-mining sediment accumulation.

Determination of detailed sedimentation rates from <sup>210</sup>Pb dating allowed calculation of copper and mercury fluxes through time. However, due to the large amount of tailings discharged into Torch Lake, the meter-length sediment cores did not penetrate all the way through the deep slime clay (tailing) layers, so the bottom record begins during the early mining period. There is a high correlation between fluxes for Cu and THg (N = 23, r = 0.834, p < 0.001), although because of greater mill discharges, fluxes for Cu are larger in Torch Lake than in Portage Lake, varying between 3 and 12,800 mg/m<sup>2</sup>/y during the early mining period and increasing to 9–56,800 mg/m<sup>2</sup>/y during the late mining period (Fig. 6). Total mercury fluxes (THg) are also higher than in Portage Lake, varying between 280 and 3070  $\mu$ g/m<sup>2</sup>/y in the early mining period and reaching maxima of 10,130–21,300  $\mu$ g/m<sup>2</sup>/y during the late mining period. During the mining era in Torch Lake, fluxes for THg reached peaks 10- to 710-fold greater than present day atmospheric deposition. That is, as in Portage Lake, there was a major increase in THg loading closely correlated with copper mining.

In Torch Lake, circumstances were more complicated than in Portage Lake, because changing mining practices influenced metal concentrations in the lake core sequence. The profiles of total Cu and THg in Torch Lake sediments show elevated concentrations in the early mining period, and relatively low concentrations in late mining era strata. Wilfley tables, combined with the second-stage grinding implemented in 1910, reduced copper and associated mercury losses in tailings by 70% (Benedict, 1955). In addition, leaching and enhanced flotation, implemented in 1914, were able to reduce metal losses an additional 20-30% (Quirk, 1999). These technological advances prompted the largest company (Calumet-Hecla) to dredge early coastal tailings piles and to re-extract copper, releasing the "double-processed tailings" back into Torch Lake. Enough additional copper was re-extracted to provide a third of Calumet-Hecla yearly profits (Benedict, 1955; Quirk, 1999). The metal-depleted tailings resulted in lower Cu and THg concentrations in late-mining era sediments relative to concentrations in the earlier period of conventional mining. We emphasize that dredging and chemical flotation techniques were not practiced in Portage Lake.



Fig. 6. Sediment profiles at 20-m site in Torch Lake. Profiles include porosity, total copper concentrations (µg/g), total mercury and methyl mercury concentrations (ng/g), ratios of methyl to total Hg (%MHg), and net accumulation rates (fluxes) for Cu and total Hg. Horizontal lines indicate the historical periods of early mining (before 1945), late mining (until 1968), and post-mining (after 1968). Copper, total mercury, and methyl mercury concentrations were depressed during the late mining interval, due to double processing of tailings (dredging old piles, using chemical flotation techniques, then slucing tailings back into lake). Despite double processing, fluxes for Cu and Hg remain greatly elevated during the late mining era (peaks > 100 times modern flux). Noteworthy is the increase in concentrations of copper, total and methyl mercury in high loss of ignition (LOI%) strata following cessation of mining.

In post-mining sediments, fluxes of both Cu and THg dramatically decline. However, the increase of THg and Cu concentrations at the base of the post-mining strata seems initially counterintuitive. Two important processes appear involved here, the first being relaxation of dilution from double-processed tailings and an increase in organic matter deposition (%LOI) as mining ceases. In addition to lateral transports of metals from covered shoreline piles, there is a postulated upward diffusion of metal-laden pore waters from the extensive buried slime clay strata, depositing metals as they come into contact with carbon-rich post-mining strata (McDonald, 2005; McDonald et al., 2010). Concentrations of metals in recent sediments remain substantially above recommended sediment quality guidelines (Buchman, 1999; Environment Canada, 2005).

In the Torch Lake core, MeHg and THg concentrations are again highly correlated (Fig. 6, regression y = 0.0017x + 0.0187; r<sup>2</sup> = .775; F = 96.2; p = 1.47xE - 10). Although early mine strata contain elevated concentrations of total mercury (502-882 ng/g, i.e. ppb), the high concentrations of both THg (451–466 ng/g) and MeHg (0.7–1.1 ng/g) found in post-mining organic-rich sediment layers are reminiscent of the peaks observed during the Depression Era and post-WWII strata in Portage Lake sediments. Methyl mercury concentrations are present at the base of the core (early mining-era sediments), decline during the late mining period, then increase to much higher concentrations (0.5-1.0 ng/g) in recent, post-mining sediments. During the late mining era, dilution from double-treated tailings again probably contributes to the mid-profile decline. MeHg/THg ratios are relatively low in early mining strata (0.02–0.03%), and increase during late-mining and postmining strata (0.2–0.3%). The sediment MeHg profiles suggest active methylation in the neighborhood, which may not be surprising because wetlands border Torch Lake on several sides.

#### Discussion

## Mining discharges into the Keweenaw Waterway

As mentioned earlier, in Portage and Torch Lake sediment profiles, exact agreement between copper and mercury fluxes was not expected since the majority of copper loading came from mill tailings, whereas the majority of mercury loading came from smelters (Kerfoot et al., 2004). However, because the copper removed from stamp sands made up the majority of copper smelted around the Keweenaw Waterway, and the mercury concentrations in copper from different mining sites were very comparable (ca. 4 ppm; Table 2), moderately strong spatial and temporal correlations between copper and THg fluxes were expected and found in long-term records (Table 4). We found other published references to mercury in Keweenaw copper and silver deposits and in Silver Islet ores (Newhouse, 1933; Wilson, 1986; Votava and Bornhorst, 2011). In Votava and Bornhorst's recent characterization of ore samples from the Caledonia Mine, Keweenaw Peninsula, the elements Cu, Hg, and Ag were strongly correlated. In particular, Hg and Ag had a rank correlation coefficient of 0.966. Native copper ore from Portage Lake Volcanic outcrops on Isle Royale has also shown evidence of trace mercury (Cannon and Woodruff, 1999). Our Portage/Torch Lake findings indicate that smelter and tailings discharges during the active mining period increased local THg deposition rates 4- to 700-fold for over a century and led to a major pulse of methylation. The existence of methyl mercury deep within the mining-era sediments of both Portage and Torch Lakes (Figs. 5,7) provides unambiguous proof that some of the mercury in the mining discharges was subject to methylation.

Recent meta-analysis of Great Lakes inland sediment cores by Drevnick et al. (2011) applied the correction: total atmospheric Hg flux = focus-corrected sediment Hg flux /  $(1 + (0.24 A_W:A_L))$ . That is, they assumed that 24% of Hg deposition to the terrestrial watershed was exported to each lake, a correction midway between the 26% found by Swain et al. (1992) and the 22% reported by Lorey and Driscoll (1999). Correcting for sediment focusing and subtracting watershed returned deposition produced median atmospheric deposition estimates that were broadly uniform across the Great Lakes Region. Median deposition rates for western (Lake Superior), central (Michigan-Huron-Erie), and eastern (Ontario-New England) watersheds were 2.6, 2.1, and 3.7  $\mu g/m^2/y$  for pre-industrial periods; 9.1, 9.1, and 13.1  $\mu$ g/m<sup>2</sup>/y for 1970; peaking at 13.1, 15.0 and 16.9  $\mu$ g/m<sup>2</sup>/y in the late 1980s, and declining to 10.3, 13.1, and 10.8  $\mu$ g/m<sup>2</sup>/y, respectively, in recent times. Again, the selected lake sites were distant from known mining emission centers ("undisturbed", "removed from industrial waste") for a better comparison with NADP regional estimates. Attempts to derive uniform regression estimates for watershed inputs were not successful, so application of the 24% value to individual watersheds was not recommended for specific cases, but used only as a general regional correction. Given the estimates, the Keweenaw Waterway loading history again emphasizes how mercury loading from copper mining discharges was 40- to 500-fold above Great Lakes Regional atmospheric deposition values, and probably underscore why THg flux values declined so rapidly once emissions ceased.

Our observed ratio of MeHg to THg of 0.2% is comparable to ratios obtained in core sediments from cold regions (Canada, Lockhart et al., 1998; Sweden, Rydberg et al., 2008; Alaska, Hammerschmidt and Fitzgerald, 2006). Moreover, in modern Lake Superior sediments, the fraction of MeHg relative to THg was found to be 4 mg/g (i.e. 0.4%; Rolfhus et al., 2003) and in L. Michigan the ratio was 3.8 mg/g (i.e. 0.38%; Mason and Sullivan, 1997). Ratios in Portage and Torch Lake sediments during the mining era resemble these values, and rise following cessation of high Cu discharges, either after mining or during the Great Depression.

We want to stress that the majority of MeHg was deposited during the mining era in both lake profiles (Portage Lake 91%; Torch Lake 76%). Under suitable conditions, MeHg can be produced within lake sediments. Examples include Boston Harbor, Massachusetts, Lake Superior, St. Lawrence River, and Saguenay Fjord in Canada (Benoit et al., 2009; Johnson et al., 2012; Fathi et al., 2013; and Gagnon et al., 1997). Yet MeHg requires special conditions for formation: availability of sulfate, suppressed oxygen levels, redox conditions, organic carbon content, low sulfur content, and non-toxic conditions for bacteria (Hollweg et al., 2009; Heyes et al., 2006; Heyes et al., 2004; Sunderland et al., 2004). Moreover, in the Tahquamenon River, a tributary to Lake Superior east of our site, Stoor et al. (2006) reported MeHg production in hyporheic environments associated with wetlands and forest. Thus MeHg measured in lake sediments may be generated within its sediments or transported to the lake via groundwater and interconnected drainage systems. Relative contributions from lakes and river drainage remain controversial. In the METAALICUS study, only a small fraction of the isotopes deposited in uplands and wetlands were found in an interconnected lake after two years, whereas the isotope delivered directly to the lake was methylated in anoxic bottom waters (Gilmour et al., 2006).

There are interesting apparent time differences in MeHg concentration profiles relative to THg flux and concentration profiles. One could argue that Hg<sup>0</sup> mercury from smelter emissions was not only deposited in the immediate Waterway vicinity, but was spread around surrounding watersheds, and similar to studies on the Tahquamenon River, might take time to cycle back via local rivers (e.g. Pike, Pilgrim, Otter, Sturgeon, Traprock) into the Keweenaw Waterway. The total accumulating in Waterway sediments would include in situ methylation from lake sediments, from bordering wetlands, plus return from the entire watershed (Swain et al., 1992; Grigal, 2002; Fitzgerald and Lamborg, 2004). The presence of appreciable total and methyl mercury in Great Depression sediments and in strata immediately after cessation of active mill and smelter discharge may suggest time lags associated with watershed methylation. The time lags would reflect the longevity of deposited Hg<sup>0</sup> in the environment, not the rapid cycling of MeHg. A few workers have tried to estimate the duration of time lags in loading to lakes from watersheds, finding that effects are generally magnified in lakes with larger watersheds (Lorey and Driscoll, 1999; Kamman and Engstrom, 2002; Harris et al., 2007).

An alternative explanation relates to Cu toxicity. Differences in timing might relate to Cu toxicity during the mining era, i.e. that methylating bacteria were suppressed in lake sediments and surrounding wetlands during high Cu fluxes. One possible way to interpret the variability is as follows: 1) at low Cu loading, methyl Hg production was limited by availability of inorganic Hg; 2) at intermediate THg loadings corresponding to the time of active mining, a lot of the scatter around the regression line likely resulted from inhibition of methylating bacteria by Cu loading in Portage and Torch Lakes (Fig. 5 and 6 profiles), such that the production of MeHg was limited by biotic factors related to methylation, rather than availability of inorganic Hg; and 3) at the highest loadings in Portage Lake (Fig. 5), high MeHg production reflected loading and the fact that these higher loadings occurred during the Depression, when Cu toxicity was lower and methylating bacteria were likely recovering and active. Thus time lags and correlated MeHg and MeHg:THg ratios may suggest that watershed microbial activity was as important as THg loading, per se. Abundant wetlands in the immediate vicinity of the Waterway were undoubtedly impacted during the copper mining era by the large amounts of copper released from mill sites. However, without further investigations, inferences of cross-interactions between copper and methylmercury production remain speculation.

In Torch Lake, vertical (diffusive) sediment transport may also be important, as 2–4 m of slime clays underlies post-mining sediments and is dewatering (McDonald et al., 2010). The Torch Lake profile has one buried peak at the depth of active surficial sediment mixing and highest concentrations at the surface. Methylation could be occurring not only at the base of the mixed layer of sediments but also at the surface, or there could be delivery of methyl mercury to the surface from the water column.

Throughout the Lake Superior watershed, there are many other mining sites where appreciable yearly mercury discharges occurred through time. Examples include: 1) the Sinter plant at Wawa, Ontario, which emitted 600 kg/y (IJC); 2) three gold mines at Hemlo, Ontario, that emitted 432–998 kg/y per mine (Hendriks and Chevalier, 2001; Kerfoot et al., 2004); 3) the White Pine smelter, MI, that emitted 635 kg/y (MDNR), and 4) taconite pellet operations in Minnesota, that emitted 200-400 kg/y total (Berndt, 2003). These yearly emissions were all relatively large, compared with modern-day calculations of basin-wide THg deposition, estimated as around 740 kg/y (Rolfhus et al., 2003). Each of the above mining operations extended for many years, yet with the exception of the Keweenaw copper and Minnesota taconite projects, no attempts have been made to calculate the longterm historical records of THg emissions or fluxes at the sites. Nor do mercury records include extensive earlier historic operations (Lake Nipigon gold fields, Wawa gold mines, Thunder Bay silver and gold mines; Kerfoot et al., 2009) where amalgamation methods were employed. Amalgamation plant sites are also known for legacy effects (Lacerda and Salomons, 1998).

Despite 45 years and 66 years, respectively, since native copper mines closed around Torch and Portage Lakes, THg concentrations in recent Torch Lake (240-650 ng/g) and Portage Lake (250-800 ng/g) sediments remain elevated above background concentrations and are at the upper end of concentration ranges reported for other lake sediments in the region. When fluxes of Hg in modern sediments of Portage  $(50-500 \ \mu g/m^2/y)$  and Torch Lakes  $(60-300 \ \mu g/m^2/y)$  are compared with fluxes in surface sediments of non-mining impacted lakes  $(5-30 \,\mu\text{g/m}^2/\text{y})$ , the Keweenaw Waterway stands out as having rates 2-16 times higher than rates in relatively undisturbed lakes. The total mercury value is only slightly less elevated than earlier estimated rates of modern-day copper flux in Portage Lake (20 times background; Kerfoot et al., 1994; Kerfoot and Robbins, 1999). With both, there are persistent elevated metal effects today in the vicinity of the Keweenaw Waterway, decades after cessation of active mining. Measured sediment focusing factors in both Portage and Torch Lake range (0.2-1.7) are not enough to account for the elevated concentrations and fluxes (Table 1; Kerfoot and Robbins, 1999; McDonald, 2005).

More information on watershed processing seems necessary to clarify exactly what is happening in the interactions between local and regional watersheds. The bioavailability of Hg is related to the fraction of total Hg present as methyl mercury, and this really reflects numerous processes, including relative rates of methylation and demethylation and relative mobilities of methyl Hg and total Hg across the watershed (Hammerschmidt and Fitzgerald, 2006). In north temperate wetland environments, factors that control the supply of MeHg to lower trophic levels seem critical, with regulatory mechanisms that include pHdependent, sulfate-dependent, or DOC-dependent Hg methylation via biotic or abiotic pathways, co-transport of Hg species and humic matter from terrestrial watersheds (Watras et al., 1995; 2006). The abundant wetlands in the Upper Peninsula are known to enhance MeHg production (e.g. Seney Tract of the eastern U.P.; St. Louis et al., 1996; Hurley et al., 1999; Stoor et al., 2006). The recovery of forest and wetlands from the mining era might actually increase MeHg production, if the number and area of wetlands increase. However, the exact geographic mix of sources (atmospheric deposition, bedrock mineral release, mining discharges) and details of watershed processing (methylation in marshes, lakes, river hyporheic systems, retention in forest soils) require additional work (MDNR, 2011). Perhaps the best approach is to advocate use of stable Hg isotopes to work out lake, wetland, and forest interactions (Tsui et al., 2012). Yet whatever the eventual details of interactions with wetlands, historic mining releases into the Keweenaw Waterway heralded the early "Industrial Revolution". Elevated mercury loadings were now part of the new way of life.

#### Acknowledgments

This study was funded in part by a Michigan Department of Environmental Quality (MDEQ) grant (Long Term Monitoring Study, Torch Lake Superfund Site) with additional support from NSF OCE 97-12872 (NOAA/NSF KITES Project) to WCK and NRU. The information in this document, especially MeHg and THg analyses, also has been funded (in part) by the U.S. Environmental Protection Agency (Ronald Rossmann). Many of the ore samples analyzed came from the A. E. Seaman Mineral Museum, Michigan Tech University, where we thank George W. Robinson for assistance. The authors gratefully acknowledge the help of Cory Larsen, Justin Massie, and Eric Sajtar with sample preparation and analysis. This is contribution number 28 of the Great Lakes Research Center at Michigan Tech.

#### References

- Appleby, P.G., Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported lead-210 to the sediment. Catena 5, 1–8.
- Benedict, C.H., 1952. Red Metal: The Calumet and Hecla Story. University of Michigan Press, Ann Arbor, Michigan.
- Benedict, C.H., 1955. Lake Superior Milling Practice. Michigan College of Mining and Technology, Houghton, Michigan.
- Benoit, J.M., Shull, D.H., Harvey, R.M., Beal, S.A., 2009. Effect of bioirrigation on sediment– water exchange of methylmercury in Boston Harbor, Massachusetts. Environ. Sci. Technol. 43 (10), 3669–3674.
- Berndt, M.E., 2003. Mercury and mining in Minnesota. Minerals Coordinating Committee, Final Report. Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, pp. 1–58.
- Bornhorst, T.J., Lankton, L.D., 2009. Copper mining: a billion years of geologic and human history. In: Schaetzl, R., Darden, J., Brandt, D. (Eds.), Michigan Geography and Geology. Pearson Custom Publishing, New York, pp. 150–173.
- Buchman, M.F., 1999. NOAA screening quick reference tables. Seattle, WA: Coastal Protection and Restoration Div., National Oceanic and Atmos. Ad., 9/99. Report No.: NOAA HAZMAT Report 99-1.
- Butler, T., Likens, G., Cohen, M., Vermeylen, F., 2007. Final Report: Mercury in the Environment and Patterns of Mercury Deposition From the NADP/MDN Mercury Deposition Network (87pp.).
- Cai, Y., Tang, R., Jaffe, R., Jones, R., 1997. Evaluation of some isolation methods for organomercury determination in soil and fish samples by capillary gas chromatography-atomic fluorescence spectrometry. Int. J. Environ. Anal. Chem. 68, 331–345.
- Cannon, W.F., Woodruff, L.G., 1999. Mercury distribution in bedrock, native copper ore, and soils—Isle Royale National Park, Michigan. Proceedings, 45th Annual Meeting of the Institute on Lake Superior Geology 45, pp. 12–13.
- Churchill, J.H., Kerfoot, W.C., 2007. The impact of surface heat flux and wind on thermal stratification in Portage Lake, Michigan. J. Great Lakes Res. 33, 143–155.

Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., et al., 2004. Modeling the atmospheric transport and deposition of mercury to the Great Lakes. Environ. Res. 95, 247–265.

Cohen, M., Draxler, R., Artz, R., 2011. Modeling atmospheric mercury deposition to the Great Lakes. Final Report (150 pp.).

- Cooke, C.A., Balcom, P.H., Kerfoot, W.C., Abbott, M.B., Wolfe, A.P., 2011. Pre-Columbian mercury pollution associated with the smelting of argentiferous ores in the Bolivian Andes. Ambio 40, 18–25.
- Diaz, J.M.L., 1973. Aqueous Environmental Chemistry of Copper and Other Heavy Metals in Torch Lake and Selected Waters of the Keweenaw Peninsula Area of Lake Superior [M.S.]. University of Wisconsin — Madison, Madison, WI.
- Drevnick, P.E., Engstrom, D.R., Driscoll, C.T., Swain, E.B., Balogh, S.J., Kamman, N.C., Long, D.T., Muir, G.C., Parsons, M.J., Rolfhus, K.R., Rossmann, R., 2011. Spatial and temporal patterns of mercury accumulation in lacustrine sediments across the Laurentian Great Lakes region. Environ. Pollut. 161, 252–260. http://dx.doi.org/10.1016/j. envpol.2011.05.025.
- Eakins, J.D., Morrison, R.T., 1978. A new procedure for the determination of lead-210 in lake and marine sediments. Int. J. Appl. Radiat. Isot. 29, 531–536.
- Engstrom, D.R., Swain, E.B., Kingston, J.C., 1985. A paleolimnological record of human disturbance from Harvey's Lake, Vermont: geochemistry, pigments and diatoms. Freshw. Biol. 15, 261–288.
- Engstrom, D.R., Balogh, S.J., Swain, E.B., 2007. History of mercury inputs to Minnesota lakes: influences of watershed disturbance and localized atmospheric deposition. Limnol. Oceanogr. 52 (6), 2467–2483.
- Environment Canada, 2000. The status of mercury in Canada. Report #2. A Background Report to the Commission for Environmental Cooperation, North American Task Force on Mercury.
- Environment Canada, 2001. Mercury: fishing for answers. Status and Trends Report #2. National Guidelines and Status Office.
- Environment Canada, 2005. Canadian environmental quality guidelines [online] Available at: http://www.ccme.ca/assets/pdf/e1\_062.pdf (Accessed 7/20/05.).
- Fathi, M., Ridal, J.J., Lean, D.R.S., Blais, J.M., 2013. Do wood fibers from a pulp mill affect the distribution of total and methyl mercury in river sediments? J. Great Lakes Res. 39, 66–73.
- Fischer, P., Gustin, M.S., 2002. Influence of natural sources on mercury in water, sediment and aquatic biota in seven tributary streams of the east fork of the Upper Carson River, California. Water Air Soil Pollut. 133 (1–2), 283–295.
- Fisher, J.A., Jacob, D.J.A.L., Soerensen, A.L., Amos, H.M., Steffen, A., Sunderland, E.M., 2012. Riverine source of Arctic Ocean mercury inferred from atmospheric observations. Nat. Geosci. 5, 499–504.
- Fitzgerald, W.F., Lamborg, C.H., 2004. Geochemistry of mercury in the environment. Treatise on Geochemistry, Environ. Geochem. vol. 9. Elsevier, pp. 107–149.
- Gagnon, C., Pelletier, E., Mucci, A., 1997. Behavior of anthropogenic mercury in coastal marine sediments. Mar. Chem. 59, 159–176.
- Gay, D., 2009. An Overview of the Mercury Deposition Network in the U.S. & Upper Midwest. Illinois State Water Survey, University of Illinois, Champaign, IL.
- Gewurtz, S.B., Shen, L., Helm, P.A., Waltho, J., Reiner, E.J., Painter, S., Brindle, I.D., Marvin, C.H., 2008. Spatial distributions of legacy contaminants in sediments of Lakes Huron and Superior. J. Great Lakes Res. 34, 153–168.
- Gilmour, C.C., Heyes, A., Mason, R.P., Rudd, J.M., 2006. Final report: response of methylmercury production and accumulation to changes in Hg loading: a wholeecosystem mercury loading study. Final Report for USEPA Grant No. R827631 (5 pp. http://cfpub.epa.gov/ncer\_abstracts/index.cfm/fuseaction/display.abstractDetail/ abstract/254/report/F, retrieved on 20 August 2015).
- Greenaway, C.M., Paterson, A.M., Keller, W., Smol, J.P., 2012. Scaled-chrysophyte assemblage changes in the sediment records of lakes recovering from marked acidification and metal contamination near Wawa, Ontario, Canada. J. Limnol. 71 (2), 267–278.
- Grigal, D.F., 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. Environ. Rev. 10, 1–39.
- Gustin, M.S., Coolbaugh, M.F., Engle, M.A., Fitzgerald, B.C., Keislar, R.E., Lindberg, S.E., et al., 2003. Atmospheric mercury emissions from mine wastes and surrounding geologically enriched terrains. Environ. Geol. 43, 339–351. http://dx.doi.org/10.1007/ s00254-002-0630-z.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Methylmercury cycling in sediments on the continental shelf of southern New England. Geochim. Cosmochim. Acta 70, 918–930. Harris, R.C., et al., 2007. Whole-ecosystem study shows rapid fish-mercury response to
- changes in mercury deposition. Proc. Natl. Acad. Sci. U. S. A. 104 (42), 16586–16591. Hendriks, D.W., Chevalier, G., 2001. Recovery of gold using gravity concentration: the
- Hemlo experience. Eur. J. Miner. Process. Environ. Prot. 208–219 (Knelsen Group, Technical Reports and Abstracts).
- Heyes, A., Miller, C., Mason, R.P., 2004. Mercury and methymercury in Hudson River sediment: impact of tidal resuspension on partitioning and methylation. Mar. Chem. 90 (1–4), 75–89.
- Heyes, A., Mason, R.P., Kim, E., Sunderland, E., 2006. Mercury methylation in estuaries: insights from using measuring rates using stable mercury isotopes. Mar. Chem. 102 (1–2), 134–147.
- Hollweg, T.A., Gilmour, C.C., Mason, R.P., 2009. Methymercury production in sediments of Chesapeake Bay and the mid-Atlantic continental margin. Mar. Chem. 114 (2–4), 86–101.
- Horvat, M., Jereb, V., Fajon, V., Logar, M., Kotnik, J., Faganell, J., Hines, M.E., Bonzongo, J.-C., 2002. Mercury distribution in water, sediment and soil in the Idrijca and SocAhca river systems. Geochem.: Explor., Environ., Anal. 2 (3), 287–296. http://dx.doi.org/ 10.1144/1467-787302-033.
- Hurley, J.P., Benoit, J.M., Babiarz, C.L., Shafer, M.M., Andren, A.W., Sullivan, J.R., et al., 1999. Influences of watershed characteristics on mercury levels in Wisconsin rivers. Environ. Sci. Technol. 29 (7), 1867–1875.

- Jeong, J., Urban, N.R., Green, S., 1999. Release of copper from mine tailings on the Keweenaw Peninsula. J. Great Lakes Res. 25, 721–734.
- Johnson, T.C., Van Alstine, J.D., Rolfhus, K.R., Colman, S.M., Wattrus, N.J., 2012. A high resolution study of spatial and temporal variability of natural and anthropogenic compounds in offshore Lake Superior sediments. J. Great Lakes Res. 38, 673–685.
- Jones, R., Jacobson, M., Jaffe, R., West-Thomas, J., Arfstrom, C., Alli, A., 1995. Method development and sample processing of water, soil, and tissue for the analysis of total and organic mercury by cold vapor atomic fluorescence spectrometry. Water Air Soil Pollut. 80 (1–4), 1285–1294.
- Kamman, N.C., Engstrom, D.R., 2002. Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from <sup>210</sup>Pb dated sediment cores. Atmos. Environ. 36, 1599–1609.
- Keeler, G.J., Dvonch, J.T., 2005. Atmospheric mercury: a decade of observations in the Great Lakes. In: Pirrone, N., Mahaffey, K.R. (Eds.), Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures Around the World. Springer Publishers, Norwell, MA, pp. 611–636.
- Kemp, A.L.W., William, J.D.H., Thomas, R.L., Gregory, M.L., 1978. Impact of man's activities on the chemical composition of the sediments of Lakes Superior and Huron. Water Air Soil Pollut. 10, 381–402.
- Kerfoot, W.C., Robbins, J.A., 1999. Nearshore regions of Lake Superior: Multi-element signatures of mining discharges and a test of Pb-210 deposition under conditions of variable sediment mass flux. J. Great Lakes Res. 25 (4), 697–720.
- Kerfoot, W.C., Lauster, G., Robbins, J.A., 1994. Paleolimnological study of copper mining around Lake Superior: artificial varves from Portage Lake provide a high resolution record. Limnol. Oceanogr. 39 (3), 649–669.
- Kerfoot, W.C., Harting, S.L., Rossmann, R., Robbins, J.A., 2002. Elemental mercury in copper, silver, and gold ores: an unexpected contribution to Lake Superior sediments with global implications. Geochem.: Explor., Environ., Anal. 2, 185–202.
- Kerfoot, W.C., Harting, S.L., Jeong, J., Robbins, J.A., Rossmann, R., 2004. Local, regional, and global implications of elemental mercury in metal (copper, silver, gold, and zinc) ores: insights from Lake Superior sediments. J. Great Lakes Res. 30 (Suppl. 1), 162–184.
- Kerfoot, W.C., Jeong, J., Robbins, J.A., 2009. Lake Superior mining and the proposed mercury zero-discharge region. In: Munawar, M., Munawar, I.F. (Eds.), State of Lake Superior. Ecovision World Monograph Series, pp. 153–216.
- Kerfoot, W.C., Yousef, F., Green, S.A., Regis, R., Shuchman, R., Brooks, C.N., Sayers, M., Sabol, B., Graves, M., 2012. Light detection and ranging (LiDAR) and multispectral studies of disturbed Lake Superior coastal environments. Limnol. Oceanogr. 57 (3), 749–771.
- Kolak, J.J., Long, D.T., Kerfoot, W.C., Beals, T.M., Eisenreich, S.J., 1999. Near-shore versus offshore copper loading in Lake Superior sediments: implications for transport and cycling. J. Great Lakes Res. 25, 611–624.
- Lacerda, L.D., Salomons, W. (Eds.), 1998. Mercury From Gold and Silver Mining: A Chemical Time Bomb?Springer, Berlin
- Lebel, J., Mergler, D., Branches, F., Lucotte, M., Amorim, M., Larribe, F., Dolbec, J., 1998. Neurotoxic effects of low-level methylmercury contamination in the Amazonian Basin. Environ. Res. Sect. A 79, 20–32.
- LECO\_Corporation, 2003. AMA254 Instruction Manual. LECO Corporation, St. Joseph, MI.

Lockhart, W.L., Wilkinson, P., Billeck, B.N., Danell, R.A., Hunt, R.V., Brunskill, G.J., Delaronde, J., Louis, V.St., 1998. Fluxes of mercury to lake sediments in central and

northern Canada inferred from dated sediment cores. Biogeochemistry 40, 163–173. Lorey, P., Driscoll, C., 1999. Historical trends of mercury deposition in Adirondack lakes. Environ. Sci. Technol. 33, 718–722.

- LSBP (Lake Superior Binational Program), 2002. Lake Superior LaMP 2002 Progress Report. LSBP (Lake Superior Binational Program), 2011. 2011 LaMP Annual Report. 1990–2010 Critical Chemicals Milestones Document.
- Lytle, R.D., 1999. In situ copper toxicity tests: applying likelihood ratio tests to *Daphnia pulex* incubations in Keweenaw Peninsula waters. J. Great Lakes Res. 25, 744–759. http://dx.doi.org/10.1016/S0380-1330(99)70774-4.
- Mason, R.P., Sullivan, K.A., 1997. Mercury in Lake Michigan. Environ. Sci. Technol. 31 (3), 942-947.
- McDonald, C.P., 2005. Historical Sedimentation Dynamics and a Model for Copper in Torch Lake, Houghton County, MI [M.S.]. Michigan Technological Univ, Houghton.

McDonald, C.P., Urban, N.R., 2007. Sediment isotope dating across a stratigraphic discontinuity in a mining-impacted lake. J. Environ. Radioact. 92, 80–95.

- McDonald, C.P., Urban, N.R., Barkach, J.H., McCauley, D., 2010. Copper profiles in the sediments of a mining-impacted lake. J. Soils Sediments. http://dx.doi.org/10.1007/ s11368-009-0171-0.
- MDNR, 2011. The Distribution of Total and Methyl Mercury in Michigan's Upper Peninsula Lakes. Michigan Department of Environmental Quality (May 2011, 79pp.).
- Murdoch, A., 1943. Boom Copper. Drier/Koepel, Calumet. Nacht, D.M., Gustin, M.S., Engle, M.A., Zehner, R.E., Giglini, A.D., 2004. Atmospheric mercu-
- ry emissions and speciation at the Sulphur Bank Mercury Mine Superfund site, northern California. Environ. Sci. Technol. 38 (7), 1977–1983.
- Newhouse, W.H., 1933. Mercury in native silver. Am. Mineral. 18, 295–296.
- Quirk, D.J., 1999. Copper From Sand: A History of Copper Reclamation on Torch Lake, Houghton County, Michigan [M.S.]. Michigan Technological University, Houghton, MI.
- Risch, M.R., Gay, D.A., Fowler, D.A., Keeler, K.K., Backus, G.J., Blanchard, S.M., Barres, P., Dvonch, J.A., J. T., 2011. Spatial patterns and temporal trends in mercury concentrations, precipitation depths, and mercury wet deposition in the North American Great Lakes Region, 2002–2008. Environ. Pollut. http://dx.doi.org/10.1016/j.envpol.2011.05.030.
- Robbins, J.A., 1978. Geochemical and geophysical applications of radioactive lead. In: Nriagu, J.O. (Ed.), Biogeochemistry of Lead In The Environment. Elsevier Scientific, Amsterdam, pp. 285–393.
- Rolfhus, K.R., Sakamoto, H.E., Cleckner, L.B., Stoor, R.W., Babiarz, C.L., Back, R.C., et al., 2003. Distribution and fluxes of total and methylmercury in Lake Superior. Environ. Sci. Technol. 37 (5), 865–872.

Rossmann, R., 1999. Horizontal and vertical distributions of mercury in 1983 Lake Superior sediments with estimates of storage and mass flux. J. Great Lakes Res. 25 (4), 683–696.

- Rydberg, J., Galman, V., Renberg, I., Bindler, R., Lambertsson, L., Martinez-Cortizas, A., 2008. Assessing the stability of mercury and methylmercury in a varved lake sediment deposit. Environ. Sci. Technol. 42 (12), 4391–4396.
- Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., Scott, C., 2004. Global source attribution for mercury deposition in the United States. Environ. Sci. Technol. 38 (2), 555–569.
- St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, C.A., Flett, K.G., Roulet, R.J., N. T., s, 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environ. Sci. Technol. 30, 2719–2729.
- Stoor, R.W., Hurley, J.P., Babiarz, C.L., Armstrong, D.E., 2006. Subsurface sources of methyl mercury to Lake Superior from a wetland-forested watershed. Sci. Total Environ. 368, 99–110.
- Sunderland, E.M., Gobas, F.A.P.C., Heyes, A., Branfireum, B.A., Bayer, A.K., Cranston, R.E., Parsons, M.B., 2004. Speciation and bioavailability of mercury in well-mixed estuarine sediments. Mar. Chem. 90 (1–4), 91–105.
- Swain, E.B., Engstrom, D.R., Bringham, M.E., Henning, T.A., Brezonik, P.L., 1992. Increasing rates of atmospheric mercury deposition in midcontinental North America. Science 257, 784–787.
- Tsui, M.T.K., Blum, J.D., Kwon, S.Y., Finlay, J.C., Balogh, S.J., Nollet, Y.H., 2012. Sources and transfers of methylmercury in adjacent river and forest food webs. Environ. Sci. Technol. 46 (20), 10957–10964.
- U.S.EPA., 2001. Baseline Study Report Torch Lake Superfund Site Houghton County, Michigan. U.S.EPA, Chicago (August 2001).
- U.S.EPA., 2003. Mercury report: 2001 toxics release inventory. Region 9 also available at http://www.epa.gov/enviro.
- U.S.EPA, 2010. EPA Fact Sheet: National Listing of Fish Advisories. U.S. Environ. Protection Agency, Washington, D.C. August 2010. Report No.: EPA-823-F-10-016.

- UNEP (United Nations Environment Programme), 2002. Global Mercury Assessment Report.
- Urban, N.R., Lu, X., Chai, Y., Apul, D.S., 2004. Sediment trap studies in Lake Superior: insights into resuspension, cross-margin transport, and carbon cycling. J. Great Lakes Res. 30, 147–161. http://dx.doi.org/10.1016/S0380-1330(04)70383-4.
- Votava, J.E., Bornhorst, T.J., 2011. Towards a geochemical characterization of native copper ores of the Keweenaw. Proceedings, Institute on Lake Superior Geology vol. 57 Ashland, Wisconsin.
- Warburton, W.L, 1987. Hydrology and Copper Budget of Torch Lake, Houghton County, Michigan [M.S.]. Michigan Technological University, Houghton, MI.
- Watras, C.J., Bloom, N.S., Hudson, R.J.M., Gherini, S., Munson, R., Claas, S.A., et al., 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes. In: Watras, C.J., Huckabee, J.W. (Eds.), Mercury Pollution: Integration and Synthesis. Lewis Publ, Ann Arbor, Michigan, pp. 153–177.
- Watras, C.J., Morrison, K.A., Host, J.S., 1995. Concentration of mercury species in relationship to other site-specific factors in the surface waters of northern Wisconsin lakes. Limnol. Oceanogr. 40 (3), 556–565.
- Watras, C.J., Morrison, K.A., Regnell, O., Kratz, T.K., 2006. The methylmercury cycle in Little Rock Lake during experimental acidification and recovery. Limnol. Oceanogr. 51 (1), 257–270.
- Wedepohl, K.H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta 59, 1217–1232.
- Wilson, A., 1986. Silver Islet. Mineral. Rec. 17 (1), 49-60.
- Wong, H.K.T., Gauthier, A., Nriagu, J.O., 1999. Dispersion and toxicity of metals from abandoned gold mine tailings at Goldenville, Nova Scotia, Canada. Sci. Total Environ. 228 (1), 35–47.
- Zhang, L., et al., 2012. Assessment of modeled mercury dry deposition over the Great Lakes region. Environ. Pollut. 161, 272–283.