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Legacy mercury releases during copper mining near Lake Superior

W. Charles Kerfoot [a,*], Noel R. Urban [b], Cory P. McDonald [b], Ronald Rossmann [c], Huanxin Zhang [d]

[a] Department of Biological Sciences and Great Lakes Research Center, Michigan Technological University, Houghton, MI 49931, USA
[b] Department of Civil & Environmental Engineering and Great Lakes Research Center, Michigan Technological University, Houghton, MI 49931, USA
[c] U.S. EPA, Mid-Continent Ecology Division, Large Lakes Research Station, Grosse Ile, MI 48138, USA
[d] Department of Geological & Mining Engineering & Sciences, Michigan Technological University, Houghton, MI 49931, USA

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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 μg/m^2/y (wet only) to 5–30 μg/m^2/y (gross deposition). Sedimentary records from scattered Michigan lakes, removed from mining sites, record around 5–24 μg/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 μg/m^2/y; peaks of 5120 to 21,300 μg/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.

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 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

* Corresponding author. Tel.: +1 906 487 2791.
E-mail address: wkerfoot@mtu.edu (W. Charles Kerfoot).

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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 $Hg_{(0)}$ 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

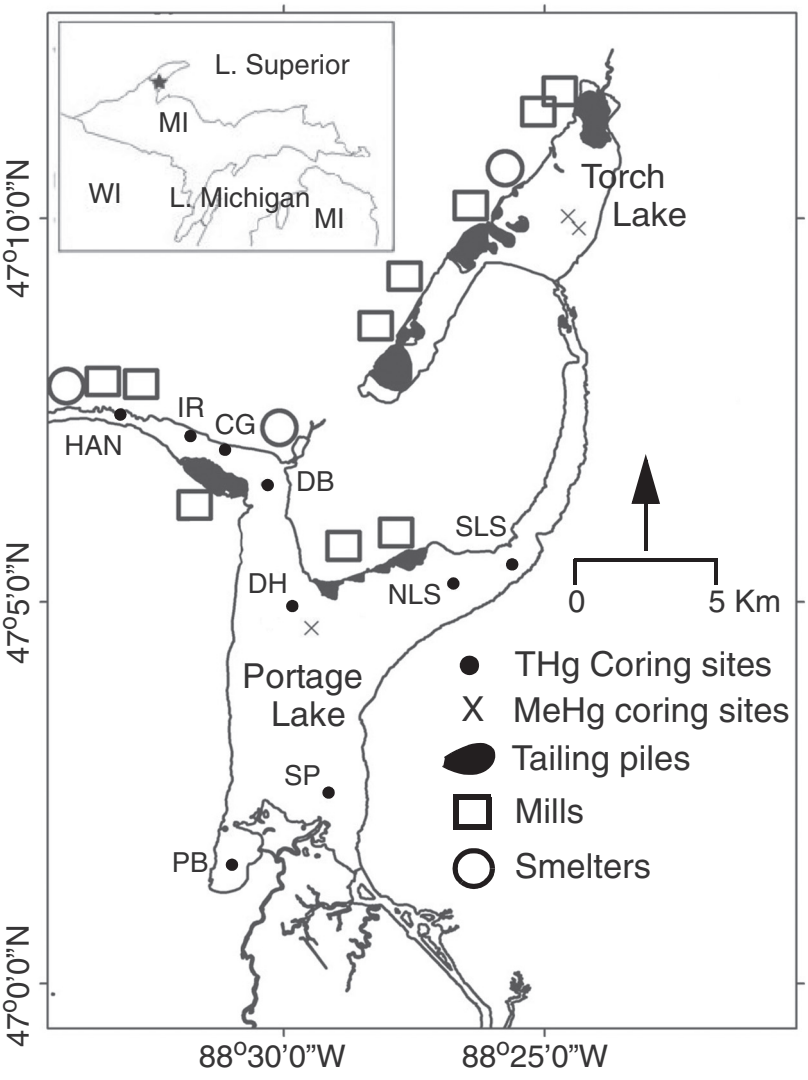

Fig. 1. Geographic position of the Keweenaw Waterway, showing coring sites. The Waterway (star) occurs midway up the Keweenaw Peninsula, a portion of the Upper Peninsula of Michigan that juts into Lake Superior. Large Xs indicate the three coring locations where we measured total and methyl Hg profiles. 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.

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