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Results of the Lake Michigan Mass Balance Study: Mercury Data Report

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Executive Summary

The U.S. Environmental Protection Agency's Great Lakes National Program Office (GLNPO) and its partners instituted the Lake Michigan Mass Balance (LMMB) Study to measure and model the concentrations of representative pollutants within important compartments of the Lake Michigan ecosystem. The goal of the LMMB Study was to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State, Tribal, and local levels. Objectives of the study were to:

1. Estimate pollutant loading rates,
2. Establish a baseline to gauge future progress,
3. Predict the benefits associated with load reductions, and
4. Further understand ecosystem dynamics.

The LMMB Study measured the concentrations of mercury, polychlorinated biphenyls (PCBs), *trans*-nonachlor, and atrazine in the atmosphere, tributaries, lake water, sediments, and food webs of Lake Michigan. This document summarizes the mercury data collected as part of the LMMB Study, and is one in a series of data reports that documents the project.

Mercury is a naturally occurring transition metal, in Group II of the periodic table, with three possible valences, or oxidation states, Hg^0, Hg^{+1}, and Hg^{+2}. The principal mineral source of mercury in the geosphere is cinnabar (HgS). Mercury also occurs as a trace element in other commercially significant geologic deposits, including coal.

Elemental mercury is commonly used in barometers and thermometers. Its high reduction potential and low resistivity make it ideal for use in battery cells, electrical switches, and fluorescent lamps. Elemental mercury or inorganic mercury compounds are used as catalysts in the oxidation of organic compounds and the production of chlorine and caustic soda. Elemental mercury is a principal component of the silver amalgam used in dental fillings. Mercury may be used in gold mining operations because it forms an amalgam with gold which then can be separated from the gold-bearing ore. Mercury compounds were used for many years as antifungal agents in interior and exterior paints and at pulp and paper mills.

Global releases of mercury to the environment come from both natural and anthropogenic (caused by human activity) sources. Many of these sources are the result of releasing geologically bound mercury to the atmosphere. Once mercury enters the atmosphere, it becomes part of a global cycle of mercury among land, water, and the atmosphere.

Study Design

In the LMMB Study, mercury was measured in atmospheric, tributary, open-lake water column, sediment, lower pelagic food web organism, and fish samples. Methylmercury, a toxic organomercury compound of environmental concern, also was measured in tributary samples. From March 1994 through October 1995, over 2300 samples were collected and analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) or cold vapor atomic absorption spectrometry (CVAA) (sediment samples only).

Atmospheric vapor, particulate, and precipitation samples were collected from five stations surrounding Lake Michigan and one background station outside the Lake Michigan basin. Tributary samples were collected from 11 rivers that flow into Lake Michigan. Open-lake water column samples were collected from 15 sampling stations in Lake Michigan, 1 station in Green Bay, and 1 station in Lake Huron. Sediment samples were collected from over 100 stations in Lake Michigan and Green Bay. Samples of particulate matter were collected in sediment traps deployed at five stations in Lake Michigan. Samples of phytoplankton and zooplankton were collected from 14 stations in Lake Michigan. Specimens of lake

trout and coho salmon were collected from eight stations in the lake and additional coho salmon were collected from a hatchery used to stock Lake Michigan.

Mercury in Atmospheric Components

Vapor-phase mercury was detected in all of the samples collected from all LMMB Study stations. Monthly composite concentrations of vapor-phase mercury ranged from 1.16 ng/m^3 at the Chiwaukee Prairie station to 2.2 ng/m^3 at the IIT Chicago station. Vapor-phase mercury results exhibited a seasonal trend, with higher concentrations occurring in summer months and lower concentrations occurring in winter months. Vapor-phase mercury concentrations varied by sampling station. The urban station at IIT Chicago had a higher mean monthly composite concentration for the duration of the study period than the urban-influenced and rural sites.

Particulate-phase mercury was detected in all of the samples collected from all LMMB Study stations. Concentrations of particulate-phase mercury in individual samples ranged from 1.05 pg/m^3 at Sleeping Bear Dunes to 494 pg/m^3 at the IIT Chicago station. Particulate-phase mercury results exhibited a seasonal trend at the Sleeping Bear Dunes station, with higher concentrations occurring in summer months and lower concentrations occurring in winter months. However, there were no statistically significant seasonal differences for the other five sampling stations. Particulate-phase mercury concentrations varied by sampling station in a manner similar to that of the vapor-phase mercury concentrations. The urban station at IIT Chicago had a higher mean monthly composite concentration for the duration of the study period than the urban-influenced and rural sites.

Mercury was detected in all of the precipitation samples collected from the LMMB Study stations. The mercury concentrations in individual samples of precipitation ranged from 2.09 ng/L at Sleeping Bear Dunes to 137 ng/L at the rural Bondville station. The differences in precipitation mercury concentrations between stations were much less significant than for the vapor-phase or particulate-phase samples. The mean concentration at Sleeping Bear Dunes was significantly lower than those at IIT Chicago, Bondville, and Chiwaukee Prairie, and the mean concentration at South Haven was significantly lower than that at IIT Chicago. Seasonal differences in precipitation mercury concentrations were less evident than for the other atmospheric phases, but summer concentrations tended to be higher than those in winter.

Mercury and Methylmercury in Tributaries

The dissolved mercury was detected in all of the samples from all of the tributaries. Dissolved mercury concentrations in individual samples ranged from 0.202 ng/L in the Kalamazoo River to 40.8 ng/L in the Fox River. The total mercury concentrations in individual samples ranged from 0.536 ng/L in the Muskegon River to 191 ng/L in the Fox River. Particulate mercury concentrations were calculated as the difference between the measured total and dissolved mercury concentrations. As a result of the low concentrations of mercury present in many samples and the uncertainties in both the total and dissolved measurement results, some of the calculated particulate mercury results were negative numbers. The highest calculated particulate mercury concentration occurred in the Fox River at 153 ng/L.

The concentrations of dissolved and total mercury exhibited seasonal trends for many of the tributaries, with higher mean concentrations occurring in the spring months and lower mean concentrations occurring in winter months. However, the seasonal trends varied by tributary and many were tied to the seasonal flow regimes in the rivers, which are dominated by high spring flows.

Methylmercury concentrations were often two orders of magnitude lower than the inorganic mercury concentrations, with many samples having no detectable methylmercury in the dissolved phase. The

seasonal trends in methylmercury concentrations varied by tributary and many were tied to the seasonal flow regimes in the rivers, which are dominated by high spring flows.

Mercury in Open-lake Water

Total and particulate mercury were detected in the majority of the samples collected from the open lake. Except for the result of a single sample collected at Station 380, there was little difference in the mean total or particulate mercury concentrations by station, nor were there any statistically significance differences between the northern and southern portions of the lake. This relatively uniform distribution of mercury within the lake is consistent with previous assessments that suggest that the primary source of mercury is atmospheric rather than riverine.

Open-lake samples were collected at depths ranging from 1 to 150 m. There was only a weak correlation between mercury concentrations and depth when the entire data set was examined. However, when only the data for the summer and autumn were used, the correlations for total and particulate mercury became stronger, as a result of the thermal stratification of the lake during these months. During periods of stratification, samples collected at depths above 40 m generally had higher mercury concentrations.

Mercury in Sediments

Mercury was detected in all of the sediment samples and all of the sediment trap samples collected during the study. Mercury concentrations in sediment samples ranged from 0.002 mg/kg to 0.260 mg/kg, while concentrations in the sediment trap samples ranged from 0.021 mg/kg to 27 mg/kg.

Sediment mercury concentrations were higher along the eastern side of the lake and higher in the deeper basins of the lake.

Mercury in Lower Pelagic Food Web Organisms

Except for one zooplankton sample, all plankton samples collected from Lake Michigan had detectable concentrations of total mercury. Total mercury concentrations in phytoplankton ranged from 10.9 to 176 ng/g. Total mercury concentrations in zooplankton ranged from 11.0 to 376 ng/g. Total mercury concentrations in zooplankton were statistically higher than those in phytoplankton.

Total mercury concentrations in zooplankton differed significantly by cruise, and were lowest in the spring, peaked in late summer, and remained elevated throughout the fall. No statistically significant differences in phytoplankton mercury concentrations were identified between cruises, although phytoplankton mercury concentrations generally increased throughout the summer and were highest in the fall.

Mercury bioaccumulation factors calculated in the LMMB Study were 1.07×10^5 for phytoplankton and 1.66×10^5 for zooplankton. These bioaccumulation factors are slightly higher than reported by other researchers for other lakes in the region. LMMB Study results indicate the biomagnification of mercury within the lower pelagic food web. Zooplankton mercury levels were significantly higher than phytoplankton mercury levels. The biomagnification factor calculated between phytoplankton and zooplankton in the LMMB Study was 1.55.

Mercury in Fish

Total mercury was detected in all of the fish samples collected for this study. Mercury concentrations in adult lake trout ranged as high as 396 ng/g and averaged 139 ng/g. In coho salmon, mercury

concentrations ranged as high as 127 ng/g and averaged 79.9, 20.6, and 69.0 ng/g in hatchery, yearling, and adult salmon, respectively. Mercury concentrations in lake trout were significantly higher than in adult or yearling coho salmon. Adult coho salmon also were significantly higher in mercury concentrations than yearling coho, which contained the lowest mean concentration of mercury.

Bioaccumulation factors were calculated as the mean dry-weight concentration in fish divided by the lake-wide mean concentration in Lake Michigan. Concentrations of total mercury in Lake Michigan fish were generally 10^5 to 10^6 times higher than total mercury concentrations in Lake Michigan water. Bioaccumulation factors were 2.18×10^5 for yearling coho salmon, 7.58×10^5 for adult coho salmon, and 1.14×10^6 for adult lake trout.

Mercury concentrations in fish averaged 139 ng/g in lake trout and 69.0 ng/g in adult coho salmon. These average values are approximately 10 times below the U.S. Food and Drug Administration's (FDA) action level of 1000 ng/g (1 ppm) for fish tissue mercury content. Even the maximum mercury concentration measured in the LMMB Study (396 ng/g) was well below the FDA action level. However, EPA guidance for fish advisories is based on the methylmercury content of fish, and methylmercury was not measured in fish in the LMMB Study. Therefore, the data from this study are not readily comparable to the EPA guidance. However, based on the conservative assumption that 100% of total mercury was in the form of methylmercury, 3% and 9% of lake trout and coho salmon, respectively, fell into the unrestricted consumption category established in the EPA guidance for methylmercury. The most contaminated coho salmon and lake trout specimens collected in the LMMB Study fell into the 4 meals/month and 2 meals/month restriction categories, respectively. For the average coho salmon sample, EPA guidance would recommend restricting consumption to 12 meals per month; and for the average lake trout sample, EPA guidance would recommend restricting consumption to 4 meals per month. This recommendation is consistent with state-wide advisories for mercury that have been issued by several states. While Lake Michigan fish mercury concentrations warrant some level of fish advisory, few fish advisories in Lake Michigan have been based solely on mercury contamination, because Lake Michigan waters are generally under more stringent fish advisories based on PCB contamination.

Mass Balance and Modeling Efforts

The data collection and quality assurance efforts described in this report were designed to support the Lake Michigan Mass Balance study and related efforts to model the concentrations of pollutants in the Lake Michigan ecosystem. However, the mass balance itself and the associated modeling efforts are beyond the scope of this data report, and will be described in later documents from GLNPO.