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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.

Chapter 1
Project Overview

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. Concentrations of polychlorinated biphenyls (PCBs), *trans*-nonachlor, atrazine, and mercury 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.

1.1 Background

The Great Lakes, which contain 20% of the world's freshwater, are a globally important natural resource that are currently threatened by multiple stressors. While significant progress has been made to improve the quality of the lakes, pollutant loads from point, non-point, atmospheric, and legacy sources continue to impair ecosystem functions and limit the attainability of designated uses of these resources. Fish consumption advisories and beach closings continue to be issued, emphasizing the human health concerns from lake contamination. Physical and biological stressors such as invasion of non-native species and habitat loss also continue to threaten the biological diversity and integrity of the Great Lakes.
The United States and Canada have recognized the significance and importance of the Great Lakes as a natural resource and have taken steps to restore and protect the lakes. In 1978, both countries signed the Great Lakes Water Quality Agreement (GLWQA). This agreement calls for the restoration and maintenance of the chemical, physical, and biological integrity of the Great Lakes by developing plans to monitor and limit pollutant flows into the lakes.

The GLWQA, as well as Section 118(c) of the Clean Water Act, required the development of Lake-wide Management Plans (LaMPs) for each Great Lake. The purpose of these LaMPs is to document an approach to reducing inputs of critical pollutants to the Great Lakes and restoring and maintaining Great Lakes integrity. To assist in developing these LaMPs and to monitor progress in pollutant reduction, Federal, State, Tribal, and local entities have instituted Enhanced Monitoring Plans. Monitoring is essential to the development of baseline conditions for the Great Lakes and provides a sound scientific base of information to guide future toxic load reduction efforts.

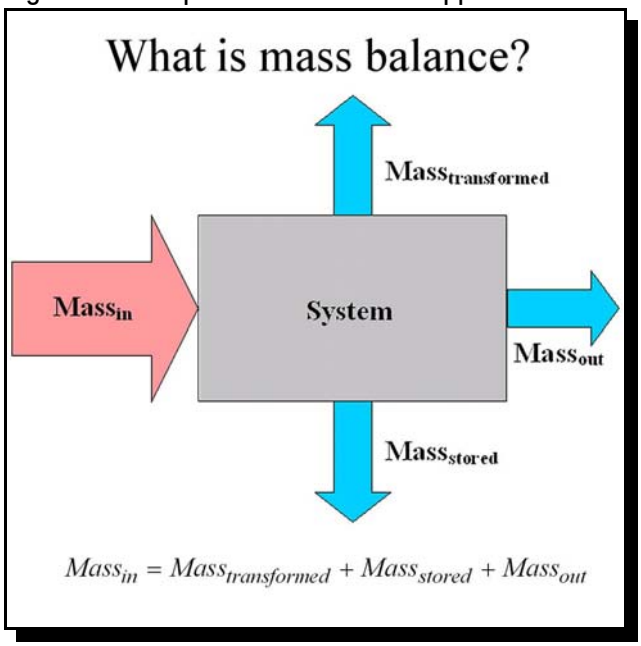
The LMMB Study is a part of the Enhanced Monitoring Plan for Lake Michigan. The LMMB Study was a coordinated effort among Federal, State, and academic scientists to monitor tributary and atmospheric pollutant loads, develop source inventories of toxic substances, and evaluate the fates and effects of these pollutants in Lake Michigan. A mass balance modeling approach provides the predictive ability to determine the environmental benefits of specific load reduction scenarios for toxic substances and the time required to realize those benefits. This predictive ability will allow Federal, State, Tribal, and local agencies to make more informed load reduction decisions.

1.2 Description

The LMMB Study used a mass balance approach to evaluate the sources, transport, and fate of contaminants in the Lake Michigan ecosystem. A mass balance approach is based on the law of conservation of mass, which states that the amount of a pollutant accumulating in a system is equal to the amount entering the system, less the amount of that pollutant leaving or chemically changed in the system (Figure 1-1).

If the system is defined as the Lake Michigan/ Green Bay water column, then pollutants may enter the system via tributaries, direct runoff, the atmosphere (wet deposition, dry deposition, and sorption from the vapor phase), the sediment, and the Straits of Mackinac. Pollutants may leave the system through volatilization to the atmosphere, loss to the sediment, or discharge through the Straits of Mackinac and the Chicago water diversion. The law of conservation of mass also can be applied to other systems such as biota, sediment, or air.

Figure 1-1. Simplified Mass Balance Approach



The LMMB Study measured contaminant concentrations in various inputs and ecosystem compartments over spatial and temporal scales. Mathematical models that track the transport and fate of contaminants within Lake Michigan are being developed and calibrated using these field data. The LMMB Study is the first lake-wide application of a mass balance determination for toxics in the Great Lakes and will serve as the basis of future mass budget/mass balance efforts.

1.3 Scope

1.3.1 Modeled Pollutants

When EPA published the *Water Quality Guidance for the Great Lakes System* (58 FR 20802), the Agency established water quality criteria for 29 pollutants. Those criteria are designed to protect aquatic life, terrestrial wildlife, and human health. PCBs, *trans*-nonachlor, and mercury are included in the list of 29 pollutants. The water quality criteria and values proposed in the guidance apply to all of the ambient waters of the Great Lakes system, regardless of the sources of pollutants in those waters. The proposed criteria provide a uniform basis for integrating Federal, State, and Tribal efforts to protect and restore the Great Lakes ecosystem.

The number of pollutants that can be intensively monitored and modeled in the Great Lakes system is limited by the resources available to collect and analyze thousands of samples, assure the quality of the results, manage the data, and develop and calibrate the necessary models. Therefore, the LMMB Study focused on constructing mass balance models for a limited group of pollutants. PCBs, *trans*-nonachlor, atrazine, and mercury were selected for inclusion in the LMMB Study because these pollutants currently or potentially pose a risk to aquatic and terrestrial organisms (including humans) in the Lake Michigan ecosystem. These pollutants also were selected to cover a wide range of chemical and physical properties and represent other classes of compounds which pose current or potential problems. Once a mass budget for selected pollutants is established and a mass balance model calibrated, additional contaminants can be modeled with limited data and future resources can be devoted to activities such as emission inventories and dispersion modeling.

1.3.1.1 Polychlorinated Biphenyls

PCBs are a class of man-made, chlorinated, organic chemicals that include 209 congeners, or specific PCB compounds. The highly stable, nonflammable, non-conductive properties of these compounds have

made them useful in a variety of products including electrical transformers and capacitors, plastics, rubber, paints, adhesives, and sealants. PCBs were produced for such industrial uses in the form of complex mixtures under the trade name "Aroclor" and were commercially available from 1930 through 1977, when EPA banned their production due to environmental and public health concerns. PCBs also may be produced by combustion processes, including incineration, and can be found in stack emissions and ash from incinerators.

Seven Aroclor formulations were included in the Priority Pollutant List developed by the EPA Office of Water under the auspices of the Clean Water Act because they were found by EPA in the effluents from one or more wastewater treatment facilities. Aroclors may have entered the Great Lakes through other means, including spills or improper disposal of transformer fluids, contaminated soils washing into the watershed, or discharges from ships. The PCBs produced by combustion processes may be released to the atmosphere, where they are transported in both vapor and particulate phases and enter the lakes through either dry deposition or precipitation events (e.g., rain).

The stability and persistence of PCBs, which made them useful in industrial applications, have also made these compounds ubiquitous in the environment. PCBs do not readily degrade and thus accumulate in water bodies and aquatic sediments. PCBs also bioaccumulate, or buildup, in living tissues. Levels of PCBs in some fish from Lake Michigan exceed U.S. Food and Drug Administration tolerances, prompting closure of some commercial fisheries and issuance of fish consumption advisories. PCBs are a probable human carcinogen, and human health effects of PCB exposure include stomach, kidney, and liver damage, liver and biliary tract cancer, and reproductive effects, including effects on the fetus after exposure of the mother.

PCB congeners exhibit a wide range of physical and chemical properties (e.g., vapor pressures, solubilities, boiling points), are relatively resistant to degradation, and are ubiquitous. These properties make them ideal surrogates for a wide range of organic compounds from anthropogenic sources.

In the LMMB Study, PCBs were selected as a model for conservative organic compounds (USEPA, 1997a).

1.3.1.2 trans-Nonachlor

trans-Nonachlor is a component of the pesticide chlordane. Chlordane is a mixture of chlorinated hydrocarbons that was manufactured and used as a pesticide from 1948 to 1988. Prior to 1983, approximately 3.6 million pounds of chlordane were used annually in the U.S. In 1988, EPA banned all production and use of chlordane in the U.S.

Like PCBs, chlordane is relatively persistent and bioaccumulative. *trans*-Nonachlor is the most bioaccumulative of the chlordanes. *trans*-Nonachlor is a probable human carcinogen. Other human health effects include neurological effects, blood dyscrasia, hepatoxicity, immunotoxicity, and endocrine system disruption.

Historically, *trans*-nonachlor may have entered the Great Lakes through a variety of means related to the application of chlordane, including improper or indiscriminate application, improper cleaning and disposal of pesticide application equipment, or contaminated soils washing into the watershed.

In the LMMB Study, *trans*-nonachlor was selected as a model for the cyclodiene pesticides (USEPA, 1997a).

1.3.1.3 Atrazine

Atrazine is a herbicide based on a triazine ring structure with three carbon atoms alternating with three nitrogen atoms. Atrazine is the most widely used herbicide in the U.S. for corn and sorghum production. Atrazine has been used as an agricultural herbicide since 1959 and 64 to 75 million pounds of atrazine are used annually in the U.S. Atrazine is extensively used in the upper Midwest, including the Lake Michigan watershed, where it is primarily associated with corn crops.

Unlike PCBs and *trans*-nonachlor, atrazine is not extremely persistent or bioaccumulative. Atrazine is moderately susceptible to biodegradation, with a half-life in soils of about 60 - 150 days. Atrazine may persist considerably longer in water and is relatively non-reactive in the atmosphere. Atrazine rarely exceeds the maximum contaminant level (MCL) set by USEPA as a drinking water standard, but localized peak values can exceed the MCL following rainfall events after atrazine application. Atrazine can cause human health effects such as weight loss, cardiovascular damage, muscle and adrenal degeneration, and congestion of heart, lungs, and kidneys. Atrazine is also toxic to aquatic plants.

In the LMMB Study, atrazine was selected as a model for reactive, biodegradable compounds in current use (USEPA, 1997A).

1.3.1.4 Mercury

Mercury is a naturally-occurring toxic metal. Mercury is used in battery cells, barometers, thermometers, switches, fluorescent lamps, and as a catalyst in the oxidation of organic compounds. Global releases of mercury in the environment are both natural and anthropogenic (caused by human activity). It is estimated that about 5,500 metric tons of mercury are released annually to the air, soil, and water from anthropogenic and natural sources (USEPA 1997b). These sources include combustion of various fuels such as coal; mining, smelting and manufacturing activities; wastewater; agricultural, animal and food wastes; chlor-alkali plants; and pulp and paper mills.

As an elemental metal, mercury is extremely persistent in all media. Mercury also bioaccumulates with reported bioconcentration factors in fish tissues in the range of 63,000 to 100,000. Mercury is a neurotoxin and possible human carcinogen and causes the following human health effects: stomach, large intestine, brain, lung, and kidney damage; blood pressure and heart rate increase, and fetus damage.

In the LMMB Study, mercury was selected as a model for bioaccumulative metals (USEPA, 1997a).

Table 1-1. Characteristics of Lake Michigan Mass Balance Modeled Pollutants

Pollutant	Sources	Uses	Toxic Effects	Biocon-centration Factor[1]	EPA Regulatory Standards[2]
PCBs	• Waste incinerators (unintentional byproducts of combustion) • Industrial dischargers • Electrical power	• Electrical transformers and capacitors • Carbonless copy paper • Plasticizers • Hydraulic fluids	• Probable human carcinogen • Hearing and vision impairment • Liver function alterations • Reproductive impairment and deformities in fish and wildlife	1,800 to 180,000	MCL = 0.5 µg/L CCC = 14 ng/L HH = 0.17 ng/L
trans-Nona-chlor[3]	• Application to crops and gardens	• Pesticide on corn and citrus crops • Pesticide on lawns and gardens	• Probable human carcinogen • Nervous system effects • Blood system effects • Liver, kidney, heart, lung, spleen, and adrenal gland damage	4,000 to 40,000	MCL = 2 µg/L CMC = 2.4 µg/L CCC = 4.3 ng/L HH = 2.1 ng/L
Atrazine	• Application to crops	• Herbicide for corn and sorghum production	• Weight loss • Cardiovascular damage • Muscle and adrenal degeneration • Congestion of heart, lungs, and kidneys • Toxic to aquatic plants	2 to 100	MCL = 3 µg/L CMC[4] = 350 µg/L CCC[4] = 12 µg/L
Mercury	• Waste disposal • Manufacturing processes • Energy production • Ore processing • Municipal and medical waste incinerators • Chlor-alkali factories • Fuel combustion	• Battery cells • Barometers • Dental fillings • Thermometers • Switches • Fluorescent lamps	• Possible human carcinogen • Damage to brain and kidneys • Adverse affects on the developing fetus, sperm, and male reproductive organs	63,000 to 100,000	MCL = 2 µg/L CMC = 1.4 µg/L CCC = 0.77 µg/L HH = 50 ng/L FWA[5] = 2.4 µg/L FWC[5] = 12 ng/L Wildlife[6] = 1.3 ng/L

[1] From: USEPA. 1995a. *National Primary Drinking Water Regulations, Contaminant Specific Fact Sheets, Inorganic Chemicals, Technical Version*. EPA 811/F-95/002-T. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.; and USEPA. 1995b. *National Primary Drinking Water Regulations, Contaminant Specific Fact Sheets, Synthetic Organic Chemicals, Technical Version*. EPA 811/F-95/003-T. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

[2] MCL = Maximum Contaminant Level for drinking water. CMC = Criterion Maximum Concentration for protection of aquatic life from acute toxicity. CCC = Criterion Continuous Concentration for protection of aquatic life from chronic toxicity. HH = water quality criteria for protection of human health from water and fish consumption. Data from: USEPA. 1999. *National Recommended Water Quality Criteria-Correction*. EPA 822/Z-99/001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

[3] Characteristics presented are for chlordane. *trans*-Nonachlor is a principle component of the pesticide chlordane.

[4] Draft water quality criteria for protection of aquatic life. From: USEPA. 2001a. *Ambient Aquatic Life Water Quality Criteria for Atrazine*. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

[5] FWA = Freshwater acute water quality criterion. FWC = Freshwater chronic water quality criterion. From National Toxics Rule (58 FR 60848).

[6] Wildlife criterion. From the Stay of Federal Water Quality Criteria for Metals (60 FR 22208), 40 CFR 131.36 and the Water Quality Guidance for the Great Lakes System (40 CFR 132).

1.3.2 Other Measured Parameters

In addition to the four chemicals modeled in the LMMB Study, many other chemicals and parameters were measured in the LMMB Study as part of the Enhanced Monitoring Program. A survey of these chemicals and parameters will aid in understanding the overall ecological integrity of Lake Michigan. These additional parameters include various biological indicators, meteorological parameters, and organic, metal, and conventional chemicals in Lake Michigan. A complete listing of all parameters included in this study is provided in Table 1-2.

Table 1-2. Lake Michigan Mass Balance Study Parameters

Organics	
acenaphthene	*p,p'*-DDT
acenaphthylene	endosulfan sulfate
aldrin	endosulfan I
anthracene	endosulfan II
atrazine	endrin
α-BHC	endrin aldehyde
β-BHC	endrin ketone
δ-BHC	fluoranthene
γ-BHC (Lindane)	fluorene
benzo [*a*] anthracene	heptachlor
benzo [*g,h,i*] perylene	heptachlor epoxide
benzo [*b*] fluoranthene	hexachlorobenzene (HCB)
benzo [*k*] fluoranthene	indeno [1,2,3-cd] pyrene
benzo [*e*] pyrene	mirex
benzo [*a*] pyrene	*trans*-nonachlor
α-chlordane	oxychlordane
γ-chlordane	PCB congeners
chrysene	phenanthrene
coronene	pyrene
p,p'-DDE	retene
p,p'-DDD	toxaphene
Metals	
aluminum	magnesium
arsenic	manganese
calcium	sodium
cadmium	nickel
chromium	lead
cesium	selenium
copper	thorium
iron	titanium
mercury	vanadium
potassium	zinc

Table 1-2. Lake Michigan Mass Balance Study Parameters

Conventionals	
alkalinity	particulate organic carbon
ammonia	percent moisture
bromine	pH
chloride	phosphorous
chlorine sulfate	silica
conductivity	silicon
dissolved organic carbon	temperature
dissolved oxygen	total Kjeldahl nitrogen
dissolved phosphorous	total organic carbon
dissolved reactive silica	total phosphorous
dry weight fraction	total suspended particulates
elemental carbon	total hardness
nitrate	turbidity
ortho-phosphorous	
Biologicals	
fish species	fish weight
fish age	fish length
fish maturity	fish taxonomy
chlorophyll *a*	fish diet analysis
fish lipid amount	primary productivity
Meteorological	
air temperature	wind direction
relative humidity	wind speed
barometric pressure	visibility
weather conditions	wave height and direction

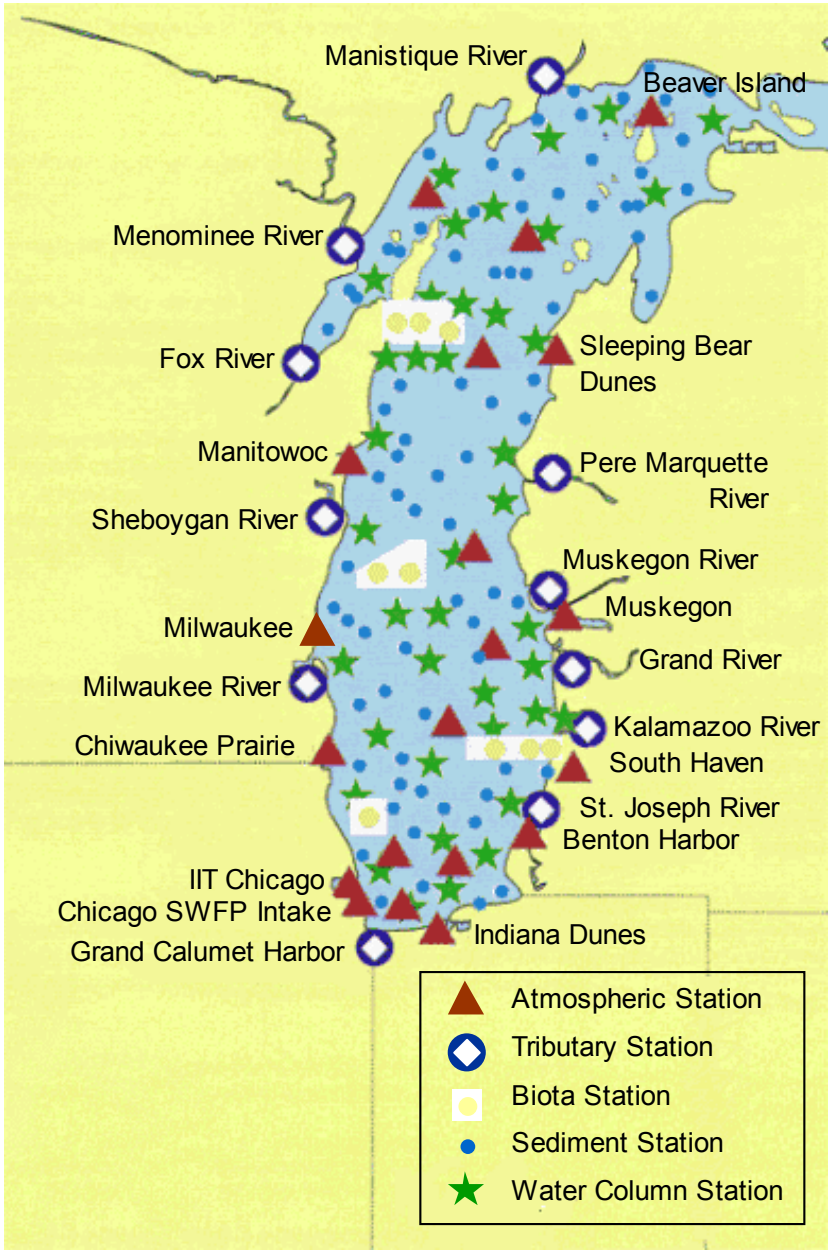
1.3.3 Measured Compartments

In the LMMB Study, contaminants were measured in the following compartments:

- **Open-Lake Water Column** — The water column in the open lake was sampled and analyzed for the modeled pollutants.
- **Tributaries** — Tributary water columns were sampled and analyzed for the modeled pollutants.
- **Fish** — Top predators and forage-base species were sampled and analyzed for diet analysis and contaminant burden. Fish were not analyzed for atrazine because atrazine is not bioaccumulative.
- **Lower Pelagic Food Web** — Phytoplankton and zooplankton were sampled and analyzed for species diversity, taxonomy, and contaminant burden. The lower pelagic food web was not analyzed for atrazine because atrazine is not bioaccumulative.
- **Sediments** — Cores were collected and trap devices were used to collect sediment for determination of contaminants and sedimentation rates. Sediments were not analyzed for atrazine because atrazine is relatively water soluble, degradable, and does not generally accumulate in sediments.
- **Atmosphere** — Vapor-, particulate-, and precipitation-phase samples were collected and analyzed for the modeled pollutants

For the modeled pollutants, more than 20,000 samples were collected and analyzed, including more than 9000 quality control (QC) samples, at more than 300 sampling locations (Figure 1-2). Field data collection activities were initially envisioned as a one-year effort. However, it became evident early into the project that a longer collection period would be necessary to provide a full year of concurrent information on contaminant loads and ambient concentrations for modeling purposes. Therefore, field sampling occurred from April 1994 to October 1995.

Figure 1-2. Lake Michigan Mass Balance Study Sampling Locations



1.4 Objectives

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. To meet this goal, the four following LMMB Study objectives were developed:

- **Estimate pollutant loading rates** — Environmental sampling of major media will allow estimation of relative loading rates of critical pollutants to the Lake Michigan Basin.
- **Establish baseline** — Environmental sampling and estimated loading rates will establish a baseline against which future progress and contaminant reductions can be gauged.
- **Predict benefits associated with load reductions** — The completed mass balance model will provide a predictive tool that environmental decision-makers and managers may use to evaluate the benefits of specific load reduction scenarios.
- **Understand ecosystem dynamics** — Information from the extensive LMMB monitoring and modeling efforts will improve our scientific understanding of the environmental processes governing contaminant cycling and availability within relatively closed ecosystems.

1.5 Design

1.5.1 Organization

The Great Lakes National Program Office proposed a mass balance approach to provide coherent, ecosystem-based evaluation of toxics in Lake Michigan. GLNPO served as the program sponsor for the LMMB Study. GLNPO formed two committees to coordinate study planning, the Program Steering Committee and the Technical Coordinating Committee. These committees were comprised of scientists from Federal, State, academic, and commercial institutions (see Section 1.5.2, Study Participants). The committees administered a wide variety of tasks including: planning the project, locating the funding, designing the sample collection, coordinating sample collection activities, locating qualified laboratories, coordinating analytical activities, assembling the data, assuring the quality of the data, assembling skilled modelers, developing the models, and communicating interim and final project results. The National Health and Environment Effects Research Laboratory (NHEERL)/Mid-Continent Ecology Division (MED)/Large Lakes and Rivers Forecasting Research Branch (LLRFRB) at Gross Ile, Michigan, in cooperation with the National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory (GLERL) and the Atmospheric Sciences Modeling Division are supporting the modeling component of the mass balance study by developing a suite of integrated mass balance models to simulate the transport, fate, and bioaccumulation of the study target analytes.

1.5.2 Study Participants

The LMMB Study was a coordinated effort among Federal, State, academic, and commercial institutions. The following agencies and organizations have all played roles in ensuring the success of the LMMB Study. Except for the three organizations indicated with an asterisk (*), all of the participants were members of the LMMB steering committee.

Federal and International

- USEPA Great Lakes National Program Office (*Program Sponsor*)
- USEPA Region 5 Water Division
- USEPA Region 5 Air Division
- USEPA Office of Research and Development (ORD) NHEERL/MED/LLRFRB
- USEPA Office of Research and Development National Exposure Research Laboratory
- U.S. Department of Interior (USDOI) U.S. Geological Survey (USGS) Water Resources Division
- USDOI USGS Biological Resources Division Great Lakes Science Center (GLSC)
- U.S. Fish and Wildlife Service (USFWS)
- U.S. Department of Commerce NOAA/GLERL
- USEPA Office of Air and Radiation*
- USEPA Office of Water*
- U.S. Department of Energy, Battelle Northwest
- Environment Canada*

State

- Illinois Department of Natural Resources
- Illinois Water Survey
- Indiana Department of Environmental Management
- Michigan Department of Environmental Quality (MDEQ)
- Wisconsin Department of Natural Resources
- Wisconsin State Lab of Hygiene

Academic and Commercial

- Indiana University
- Rutgers University
- University of Maryland
- University of Michigan
- University of Minnesota
- University of Wisconsin
- Grace Analytical

1.5.3 Workgroups

Eleven workgroups were formed to provide oversight and management of specific project elements. The workgroups facilitated planning and implementation of the study in a coordinated and systematic fashion. The workgroups communicated regularly through participation in monthly conference calls and annual "all-hands" meetings. Workgroup chairs were selected and were responsible for managing tasks under the purview of the workgroup and communicating the status of activities to other workgroups. The workgroups and workgroup chairs are listed below.

- Program Steering Committee — Paul Horvatin (USEPA/GLNPO)
- Technical Coordinating Committee — Paul Horvatin (USEPA/GLNPO)
- Modeling Workgroup — William Richardson (USEPA/ORD/NHEERL/MED/LLRFRB)
- Air Monitoring Workgroup — Jackie Bode (USEPA/GLNPO)
- Biota Workgroup — Paul Bertram (USEPA/GLNPO) and John Gannon (USDOI/USGS/GLSC)
- Chemistry Workgroup — David Anderson (USEPA/GLNPO)
- Data Management Workgroup — Kenneth Klewin and Philip Strobel (USEPA/GLNPO)

- Lake Monitoring Workgroup — Glenn Warren (USEPA/GLNPO)
- Tributary Monitoring Workgroup — Gary Kohlhepp (USEPA Region 5 Water Division) and Robert Day (Michigan Department of Environmental Quality)
- Quality Assurance Workgroup — Louis Blume and Michael Papp (USEPA/GLNPO)
- Sediment Monitoring Workgroup — Brian Eadie (NOAA/GLERL)

1.5.4 Information Management

As program sponsor, GLNPO managed information collected during the LMMB Study. Principal investigators (PIs) participating in the study reported field and analytical data to GLNPO. GLNPO developed a data standard for reporting field and analytical data and a database for storing and retrieving study data. GLNPO also was responsible for conducting data verification activities and releasing verified data to the study modelers and the public. The flow of information is illustrated in Figure 1-3.

1.5.4.1 Data Reporting

More than twenty organizations produced LMMB data through the collection and analysis of more than 20,000 samples. In the interest of standardization, specific formats (i.e., file formats and codes to represent certain data values) were established for reporting LMMB data. Each format specified the "rules" by which data were submitted, and, in many cases, the allowable values by which they were to be reported. The data reporting formats were designed to capture all pertinent sampling and analytical information from the field crews and laboratory analysts. Data reporting formats and the resulting Great Lakes Environmental Monitoring Database (GLENDA, see Section 1.5.4.2,) were designed to be applicable to projects outside the LMMB as well. For the LMMB Study, special conditions were applied for reporting analytical results. Because the data were being used for input to study models, principal investigators were asked to report analytical results as measured, even when measurements were below estimated detection limits. The quality assurance program discussed in Section 1.5.5 included identifying (i.e., flagging) all analytical results that were below estimated detection limits.

Principal investigators (including sampling crews and the analytical laboratories) supplied sample collection and analysis data following the standardized reporting formats if possible. LMMB data were then processed through an automated SAS-based data verification system, the Research Data Management and Quality Control System (RDMQ), for quality assurance/quality control checking. After verification and validation by the PI, the data sets were output in a form specific for upload to GLENDA. Finally, these data sets were uploaded to GLENDA.

1.5.4.2 Great Lakes Environmental Monitoring Database

Central to the data management effort is a computerized database system to house LMMB Study and other project results. That system, the Great Lakes Environmental Monitoring Database (GLENDA), was developed to provide data entry, storage, access and analysis capabilities to meet the needs of mass balance modelers and other potential users of Great Lakes data.

Development of GLENDA began in 1993 with a logical model based on the modernized STORET concept and requirements analysis. GLENDA was developed with the following guiding principles:

- **True multi-media scope** — water, air, sediment, taxonomy, fish tissue, fish diet, and meteorology data can all be housed in the database
- **Data of documented quality** — data quality is documented by including results of quality control parameters

- **Extensive contextual indicators** — ensures data longevity by including enough information to allow future or secondary users to make use of the data
- **Flexible and expandable** — the database is able to accept data from any Great Lakes monitoring project
- **National compatibility** — GLENDA is compatible with STORET and allows ease of transfer between these large databases

In an effort to reduce the data administration burden and ensure consistency of data in this database, GLNPO developed several key tools. Features including standard data definitions, reference tables, standard automated data entry applications, and analytical tools are (or will soon be) available.

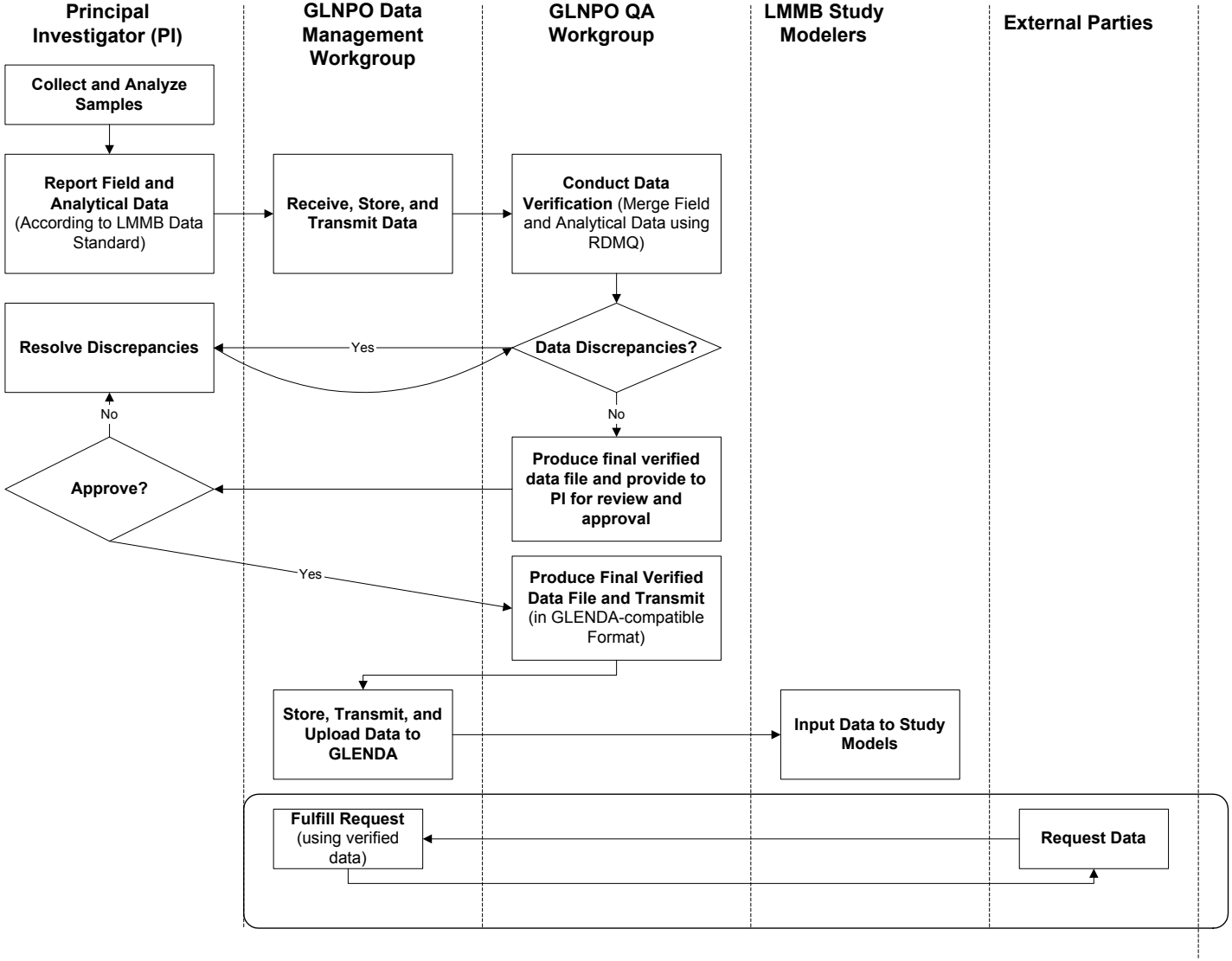
1.5.4.3 Public Access to LMMB Data

All LMMB data that have been verified (through the QC process) and validated (accepted by the PI) are available to the public. Currently, GLNPO requires that written requests be made to obtain LMMB data. The data sets are available in several formats including WK1, DBF, and SD2. More information about the data sets is available on the LMMB web site at: http://www.epa.gov/glnpo.

The primary reason for requiring an official request form for LMMB data is to keep track of requests. This allows GLNPO to know how many requests have been made, who has requested data, and what use they intend for the data. This information assists GLNPO in managing and providing public access to Great Lakes data and conducting public outreach activities. As of November 2000, 38 requests for LMMB data have been made: 8 from EPA, 5 from other federal agencies, 5 from state agencies, 5 from universities, 10 from consultants, 3 from international agencies, and 2 from non-profit or other groups. In the future, after all data are verified and validated, GLNPO intends to make condensed versions of the data sets available on the LMMB web site for downloading. This will allow easy public access to LMMB data.

Additional details of the information management for the LMMB Study can be found in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

Figure 1-3. Flow of Information in the Lake Michigan Mass Balance Study



1.5.5 Quality Assurance Program

At the outset of the LMMB Study, managers recognized that the data gathered and the models developed from the study would be used extensively by decision makers responsible for making environmental, economic, and policy decisions. Environmental measurements are never true values and always contain some level of uncertainty. Decision makers, therefore, must recognize and be sufficiently comfortable with the uncertainty associated with data on which their decisions are based. In recognition of this requirement, LMMB Study managers established a QA program goal of ensuring that data produced under the LMMB Study would meet defined standards of quality with a specified level of confidence.

The QA program prescribed minimum standards to which all organizations collecting data were required to adhere. Data quality was defined, controlled, and assessed through activities implemented within various parameter groups (e.g., organic, inorganic, and biological parameters). QA activities included the following:

- **QA Program** — Prior to initiating data collection activities, plans were developed, discussed, and refined to ensure that study objectives were adequately defined and to ensure that all QA activities necessary to meet study objectives were considered and implemented.
- **QA Workgroup** — EPA established a QA Workgroup whose primary function was to ensure that the overall QA goals of the study were met.
- **QA Project Plans (QAPPs)** — EPA worked with PIs to define program objectives, data quality objectives (DQOs), and measurement quality objectives (MQOs) for use in preparing QAPPs. Principal investigators submitted QAPPs to EPA for review and approval. EPA reviewed each QAPP for required QA elements and soundness of planned QA activities.
- **Training** — Before data collection activities, PIs conducted training sessions to ensure that individuals were capable of properly performing data collection activities for the LMMB Study.
- **Monthly Conference Calls and Annual Meetings** — EPA, PIs, and support contractors participated in monthly conference calls and annual meetings to discuss project status and objectives, QA issues, data reporting issues, and project schedules.
- **Standardized Data Reporting Format** — Principal investigators were required to submit all data in a standardized data reporting format that was designed to ensure consistency in reporting and facilitate data verification, data validation, and database development.
- **Intercomparison Studies** — EPA conducted studies to compare performance among different PIs analyzing similar samples. The studies were used to evaluate the comparability and accuracy of program data.
- **Technical Systems Audits** — During the study, EPA formally audited each PI's laboratory for compliance with their QAPPs, the overall study objectives, and pre-determined standards of good laboratory practice.
- **Data Verification** — PIs and EPA evaluated project data against pre-determined MQOs and DQOs to ensure that only data of acceptable quality would be included in the program database.
- **Statistical Assessments** — EPA made statistical assessments of the LMMB Study data to estimate elements of precision, bias, and uncertainty.
- **Data Validation** — EPA and modelers are evaluating the data against the model objectives.

Comparability of data among PIs participating in the LMMB Study was deemed to be important for successful completion of the study. Therefore, measurement quality objectives (MQOs) for several data attributes were developed by the PIs and defined in the QAPPs. MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs.

MQOs were defined in terms of six attributes:

- **Sensitivity/Detectability** — The determination of the low-range critical value that a method-specific procedure can reliably discern for a given pollutant. Sensitivity measures included, among others, method detection limits (MDLs) as defined at 40 CFR Part 136, system detection limits (SDLs), or instrument detection limits (IDLs).
- **Precision** — A measure of the degree to which data generated from replicate or repetitive measurements differ from one another. Analysis of duplicate samples was used to assess precision.
- **Bias** — The degree of agreement between a measured and actual value. Bias was expressed in terms of the recovery of an appropriate standard reference material or spiked sample.
- **Completeness** — The measure of the number of samples successfully analyzed and reported compared to the number that were scheduled to be collected.
- **Comparability** — The confidence with which one data set can be compared to other data sets.
- **Representativeness** — The degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

The PI-defined MQOs also were used as the basis for the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for conducting review of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If a result failed to meet predefined criteria, the QC Coordinator contacted the PI to discuss the result, verify that it was correctly reported, and determine if corrective actions were feasible. If the result was correctly reported and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Data that met all predefined requirements were flagged to indicate that the results had been verified and were determined to meet applicable MQOs. In this way, every data point was assigned one or more validity flags based on the results of the QC checks. GLNPO also derived data quality assessments for each LMMB Study data set for a subset of the attributes listed above, specifically sensitivity, precision, and bias. The LMMB Study modelers and the Large Lakes Research Station Database Manager also perform data quality assessments prior to inputting data into study models. Such activities include verifying the readability of electronic files, identifying missing data, checking units, and identifying outliers. A detailed description of the quality assurance program is included in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of quality implementation and assessment is provided in each of the following chapters.

1.6 Project Documents and Products

During project planning, LMMB participants developed study tools including work plans, a methods compendium, quality assurance project plans, and data reporting standards. Through these tools, LMMB participants documented many aspects of the study including information management and quality assurance procedures. Many of these documents are available on GLNPO's website at: http://www.epa.gov/glnpo/lmmb.

LMMB Work Plan

Designers of the LMMB Study have documented their approach in a report entitled *Lake Michigan Mass Budget/Mass Balance Work Plan* (USEPA, 1997a). The work plan describes the essential elements of a mass balance study and the approach used to measure and model these elements in the Lake Michigan

system. This document was developed based upon the efforts of many Federal and State scientists and staff who participated in the initial planning workshop, as well as PIs.

Quality Assurance Program/Project Plans
The Lake Michigan Mass Balance Project Quality Assurance Plan for Mathematical Modeling, Version 3.0 (USEPA, 1998) documents the quality assurance process for the development and application of LMMB models, including hydrodynamic, sediment transport, eutrophication, transport chemical fate, and food web bioaccumulation models.

The Enhanced Monitoring Program Quality Assurance Program Plan
The Enhanced Monitoring Program Quality Assurance Program Plan (USEPA, 1997c) was developed in 1993 to ensure that data generated from the LMMB Study supports its intended use.

LMMB Methods Compendium
The *Lake Michigan Mass Balance Project (LMMB) Methods Compendium* (USEPA, 1997d, 1997e) describes the sampling and analytical methods used in the LMMB Study. The entire three volumes are available on GLNPO's website mentioned above.

LMMB Data Reporting Formats and Data Administration Plan
Data management for the LMMB Study was a focus from the planning stage through data collection, verification, validation, reporting, and archiving. The goal of consistent and compatible data was a key to the success of the project. The goal was met primarily through the development of standard formats for reporting environmental data. The data management philosophy is outlined on the LMMB website mentioned above.

Lake Michigan LaMP
"Annex 2" of the 1972 Canadian-American Great Lakes Water Quality Agreement (amended in 1978, 1983, and 1987) prompted development of Lakewide Area Management Plans (LaMPs) for each Great Lake. The purpose of these LaMPs is to document an approach to reducing input of critical pollutants to the Great Lakes and restoring and maintaining Great Lakes integrity. The Lake Michigan LaMP calls for basin-wide management of toxic chemicals.

GLENDA Database
Central to the data management effort is a computerized data system to house Lake Michigan Mass Balance and other project results. That system, the Great Lakes Environmental Monitoring Database (GLENDA), was developed to provide data entry, storage, access and analysis capabilities to meet the needs of mass balance modelers and other potential users of Great Lakes data.

LMMB Data Reports
This report is one in a series of data reports that summarize the data from monitoring associated with EPA's Lake Michigan Mass Balance Study. In addition to this data report on mercury, data reports are being published for atrazine (USEPA, 2001c) and PCBs and *trans*-nonachlor (USEPA, 2004).

Future Documents and Products
Following the completion of modeling efforts associated with the LMMB Study, GLNPO anticipates publishing reports summarizing the modeling results. In 2005, GLNPO also anticipates conducting a reassessment of Lake Michigan to calibrate and confirm modeling results with data collected 10 years after the initial LMMB sampling.

Chapter 2
Mercury Study Overview

2.1 Mercury Introduction

2.1.1 Physical/Chemical Properties

Mercury is a naturally occurring transition metal, in Group II of the periodic table, along with zinc and cadmium. The atomic number for mercury is 80 and its atomic weight is 200.59 g/mole. Mercury is the only metal that occurs in a liquid state at typical environmental temperatures. The melting point of mercury is -39.87 °C, and its boiling point is 356.58 °C. Mercury has a density of 13.59 g/cm^3 and a vapor pressure of 0.00185 mm at 25 °C.

The solubility of mercury in water is approximately 0.28 µmoles/L (56.2 µg/L) at 25 °C. Its electrical resistivity is 95.76 µohm-cm at 20 °C, making it an excellent electrical conductor. In fact, the value of the ohm is formally defined on the basis of the resistance of a column of mercury of specific dimensions.

Mercury occurs naturally in the environment 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 is extracted from this ore by roasting in an oxygen atmosphere to produce elemental mercury, which can be further purified by distillation. Mercury also occurs as a trace element in other commercially significant geologic deposits, including coal.

The reduction potential is 0.851 volts for the reaction:

$$Hg^{+2} + 2e^- \leftrightarrow Hg^0$$

and 0.796 volts for the reaction:

$$Hg_2^{+2} + 2e^- \leftrightarrow 2Hg^0$$

placing mercury higher on the redox scale than most other metals.

2.1.2 Mercury Production, Uses, and Releases

Because it is a dense liquid at typical environmental temperatures and responds in a predictable fashion to changes in temperature and pressure, 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 is also used as a catalyst 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. It has been used in chlor-alkali plants around the world. Historically, mercury compounds have been used in medicinal products, including topical disinfectants such as Mercurochrome, and as a preservative in some vaccines and cosmetics. For many years, mercuric chloride was used as a biocide to preserve water samples collected for analyses of other environmental contaminants. Mercury compounds were used for many years as antifungal agents in interior and exterior paints and at pulp and paper mills.

According to the U.S. Geological Survey (USGS), there have been no domestic mines producing mercury as a primary product since 1990 (USGS, 1999). Virtually all domestic mercury production involves recovery or recycling of mercury from secondary sources such as spent batteries, mercury-containing lamps, switches, dental amalgams, and wastes from laboratories and electrolytic processes.

Data from USGS for the period from 1995 to 1999 indicate that domestic production of mercury (from secondary sources), as well as imports and exports of mercury, and industrial consumption of mercury declined. In addition, world-wide mine production declined by approximately 40% over the same period, from 3,190 to 1,970 metric tons. USGS estimated that domestic industrial consumption of mercury in 1997 was 346 metric tons (762,800 pounds). Data from EPA's Toxics Release Inventory (TRI) for 1997 indicate that 73,334 pounds of mercury (≈10% of domestic production) were released to the environment by facilities that were required to report releases to EPA. According to USGS, electrolytic production of chlorine and caustic soda account for roughly half of the domestic use of mercury, with electrical applications and products accounting for another 25%.

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. In its 1997 Report to Congress on mercury, EPA estimated that the global mercury cycle involved the release of 5,500 metric tons (12,130,000 pounds) of mercury to the atmosphere from all natural and anthropogenic sources world-wide (USEPA, 1997b). Of that total, EPA estimated that 158 metric tons (348,300 pounds) were contributed from anthropogenic sources in the U.S. in 1994 - 1995, representing about 3% of the total global mercury input to the atmosphere. Of that 158 metric tons, approximately 87% came from combustion sources, and approximately 10% came from manufacturing sources. A breakdown of these 1994 - 1995 anthropogenic emission estimates includes:

- Combustion sources (87%)
  - Coal-fired utility boilers (32.6%)
  - Municipal waste combustors (18.7%)
  - Commercial/industrial boilers (17.9%)
  - Medical waste incinerators (10.1%)
  - Hazardous waste combustors (4.4%)
  - All other combustion sources (3.3%)
- Manufacturing sources (10%)
  - Chlor-alkali plants (4.5%)
  - Portland cement kilns - excludes those that burn hazardous waste (3.1%)
  - All other manufacturing sources (2.4%)

Although it does not involve quantities of mercury similar to those used on an industrial scale, elemental mercury is used in various cultural and religious practices of some Caribbean and Latin American immigrants to the U.S., which may result in exposures that exceed current occupational standards (Riley, *et al.*, 2001). Frequently reported uses of mercury in such practices include those designed to bring luck or ward off evil by:

- Carrying a capsule, vial, or pouch containing elemental mercury on one's person
- Sprinkling it in a home or car
- Mixing it with perfume
- Burning a candle laced with mercury

Elemental mercury has also been used as a folk medicine treatment for gastroenteritis among some Mexican Americans.

In another study of such cultural and religious practices, Johnson (1999) reported that 64% of the mercury users in that study in New York City dispose of mercury by throwing it in the trash, 27% flushed used mercury down the toilet, and 9% disposed of mercury outdoors. Therefore, although the overall quantities of mercury used in these cultural practices may pale in comparison to industrial uses, the uncontrolled disposal practices could make such cultural uses significant sources of mercury to local environments.

2.1.3 Regulatory Background

Efforts in the U.S. to regulate releases of mercury to the environment began shortly after the formation of EPA in 1970. EPA regulates mercury under a wide range of environmental statutes. By 1976, the Office of Water listed mercury as one of the 129 pollutants in the consent decree that resulted from *NRDC v. Train (8 ERC 2120, 1976)*. As a result, mercury is regulated in effluent guidelines developed under the Clean Water Act and administered through the National Pollutant Discharge Elimination System (NPDES). The Office of Water has established water quality criteria (WQC) for freshwater and marine systems. The freshwater chronic WQC is 0.012 µg/L of mercury. The freshwater acute WQC is 2.1 µg/L. The WQC for human health is 0.05 µg/L.

Under the Safe Drinking Water Act, EPA established a maximum contaminant level (MCL) of 2 µg/L in 1992. Under the auspices of the Resource Conservation and Recovery Act (RCRA), EPA placed mercury on Appendix VIII (hazardous substances) and Appendix IX (groundwater monitoring), and established a Universal Treatment Standard (UTS) of 25 µg/L of mercury in non-wastewaters when subjected to the toxicity characteristic leaching procedure (TCLP) and 150 µg/L in wastewaters. Mercury is included in the Toxics Release Inventory (TRI) developed under the Emergency Planning and Community Right to Know Act (EPCRA).

The use of mercury in paints was discontinued in 1991 under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Registrations of the last two mercury-based pesticides (Calochlor and Calogran) were voluntarily cancelled by the manufacturer in 1993. In 1996, Congress enacted the Mercury-Containing and Rechargeable Battery Management Act to phase out the use of mercury in batteries. The Act limits the mercury content of "button" batteries to 25 mg per battery, prohibits the sale of most other types of batteries containing mercury, and requires that manufacturers identify suitable recycling facilities for any mercuric-oxide batteries it sells.

Mercury and mercury compounds are classified as hazardous air pollutants (HAPs) under the Clean Air Act, and EPA has established national emission standards for mercury in five source categories: ore processing facilities, mercury cell chlor-alkali plants, sewage sludge drying operations, municipal waste combustors, and medical waste incinerators.

Discharges of mercury have been significantly limited under the Great Lakes Initiative (GLI), in recognition of the impact of mercury on the Great Lakes ecosystem and the associated effects on human health in the region. In 1995, EPA issued GLI guidance that recommends that a water quality criterion of 1.8 ng/L (0.0018 µg/L) for dissolved mercury for the protection of human health (FR Vol. 60 No. 56, March 23, 1995, pp. 15366-15425).

Under the Federal Food, Drug, and Cosmetic Act, the Food and Drug Administration (FDA) banned most uses of mercury in over the counter medications and limited the concentrations of mercury used as preservatives in eye-area cosmetics. The FDA also regulates the use of mercury in dental amalgams, classifying the silver-mercury alloy as a Class II medical device, thereby subjecting it to additional controls and imposing safety regulations on its use and disposal.

2.1.4 Fate and Effects

Unlike synthetic organic contaminants, mercury is a naturally occurring element, and therefore it cannot be created or destroyed by chemical, biological, or physical processes. Rather, mercury can be transformed by oxidation or reduction reactions, or it can combine with other elements to form inorganic or organic mercury compounds. The organomercury compounds are characterized by a covalent bond between the mercury atom and a carbon atom, making mercury unusual among metals (but not unique), in that many metals form only ionic bonds with other elements.

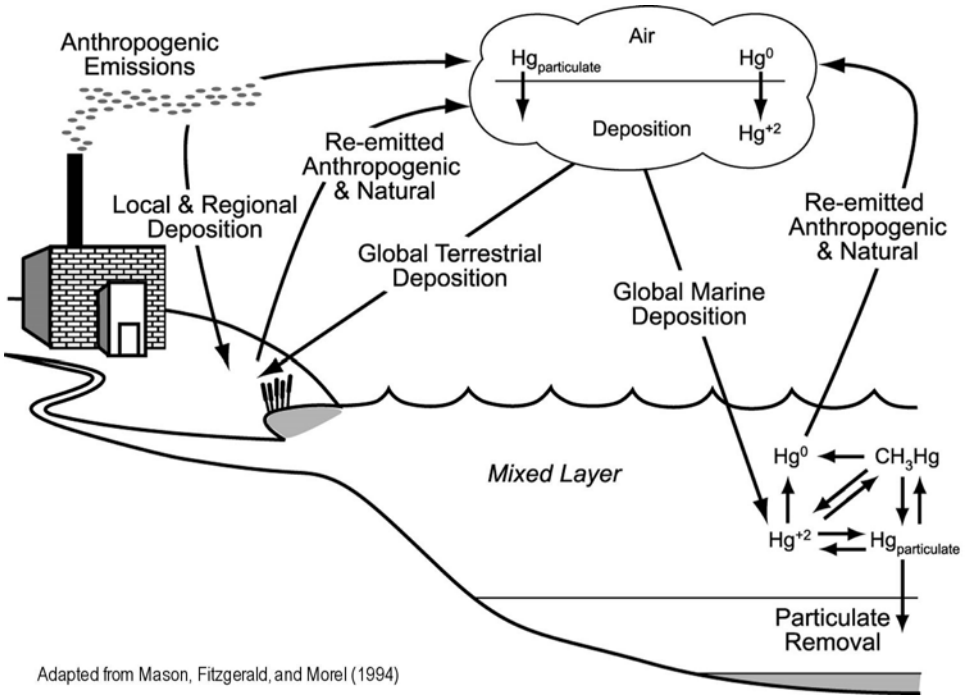
The following are the mercury compounds most likely to be found under environmental conditions: mercuric chloride ($HgCl_2$), mercuric hydroxide (Hg $[OH]_2$), mercuric sulfide (HgS), methylmercuric chloride (CH_3HgCl), methylmercuric hydroxide (CH_3HgOH), and dimethyl mercury ($[CH_3]_2Hg$) (USEPA, 1997b).

Due to the volatility of elemental mercury, the atmosphere is both an important reservoir and a major component of the global mercury cycle. That global cycle encompasses the flux of mercury in its many forms to and from the atmosphere, fresh and marine water bodies, and the land. The cycle includes a natural component that is the result of mercury that originated in geologic deposits and that has been released from those deposits by natural processes. The cycle has been significantly perturbed or modified by human activities, and includes both regional and local sources and sinks of various forms of mercury.

Although a detailed discussion of the global mercury cycle is beyond the scope of this report, in general terms, the cycle (Figure 2-1) is characterized by the following exchanges and transformations of mercury:

- Volatilization from land-based sources to the atmosphere
- Volatilization from marine-based sources to the atmosphere
- Deposition from atmosphere to land, oceans, and other water bodies
- Anthropogenic inputs of gaseous and particulate forms of mercury to the atmosphere from combustion processes and municipal and industrial sources on land
- Run-off of natural and anthropogenic mercury from land to freshwaters and oceans
- Exchanges between dissolved and particulate forms of mercury in oceans and lakes
- Exchanges of mercury between inorganic and organic forms in the water and sediments of oceans and lakes
- Deposition of mercury in sediments of oceans and lakes
- Local and regional deposition of mercury from anthropogenic combustion sources and municipal and industrial sources

Figure 2-1. Global Mercury Cycle



The residence time of elemental mercury in the atmosphere is estimated to be about one year (EPA, 1997b). As a result, mercury entering the atmosphere from any given source may be distributed globally, making mercury a ubiquitous contaminant.

2.1.5 Biological Transformations

Mercury enters the food web primarily through aquatic systems, where it is associated with dissolved and particulate forms of organic carbon (DOC and POC), and where it may undergo methylation by bacteria in sediments or in the water column to form methylmercury (USEPA, 1997b). Methylmercury accumulates in the tissues of aquatic organisms and methylmercury concentrations are magnified in aquatic food webs, with highest concentrations often found in the top predators, including many game fish. As a result, human exposure pathways related to terrestrial plants and grazing animals are much less important than pathways related to consumption of fish (USEPA, 1997b).

2.1.6 Toxicity

The effects of mercury exposure on organisms depend on the route of exposure and the form of mercury. Many people are familiar with the "Mad Hatter" in Lewis Carroll's "Alice in Wonderland," whose madness described the results of exposure of hatmakers to the mercuric nitrate used to shrink felt for hats. While the etymology of the expression "mad as a hatter" is apparently subject to some debate, the effects of exposure to elemental mercury vapors and/or soluble mercury salts were documented at the time. The "Danbury shakes" was the name given to the neurological effects exhibited by hatmakers in Danbury, Connecticut, in the 19th century.

Whether the route of exposure is through inhalation, dermal exposure, ingestion of food, or other means, mercury and mercury compounds are readily transported throughout humans and animals by blood circulation. Elemental mercury dissolved in the blood can cross the blood/brain barrier, where it can accumulate in nerve tissue. Symptoms of chronic exposure to mercury vapors include: excitability,

confusion and mental instability, personality changes, and fine tremors in the extremities. Mercury can cause kidney damage, as the kidneys works to remove mercury from the bloodstream.

The effects of organomercury compounds, particularly methylmercury and dimethylmercury, are more severe than for elemental mercury, given equivalent exposures or doses. Methylmercury is known to have teratogenic effects in the children of mothers exposed to this organomercury compound. Mild maternal exposures cause mainly neurological effects in the children, including developmental delays, reduced intelligence, and altered muscle reflexes.

Much of the data on the direct effects of elemental and organomercury exposure are the result of studies of long-term exposures of the people living around Minamata Bay, on the western coast of Kyushu, in Japan. Beginning in 1956, a series of patients were identified as exhibiting symptoms of severe convulsions, intermittent loss of consciousness, altered mental state, and ultimately permanent coma and death. The common link among the patients was that they consumed large quantities of fish from Minamata Bay. A second outbreak of what became known as "Minamata disease" occurred in 1965 when patients with the same symptoms were identified near Niigata City, far from Minamata. The affected individuals were all fishermen living along the Agano River. In these cases, methylmercury was identified in both the local fish that the patients consumed as well as in tissues from the patients' bodies.

Ultimately, the Japanese government publicly acknowledged that Minamata disease resulted from environmental pollution. The source of the pollution in Minamata Bay was the untreated effluent from the Nippon Chisso chemical manufacturing plant in Minamata City. Nippon Chisso produced acetaldehyde and polyvinyl chloride (PVC) at the Minamata plant, and used large quantities of inorganic mercury compounds as reaction catalysts. Although most of the mercury was recovered within the plant, massive amounts were discharged in the wastewater over a period of decades, and much of it accumulated in the sediments and biota of the bay. The methylmercury found in fish from the Agano River was ultimately traced to the Showa Denko Company facility in Kase, on the upper reaches of the river (Ui, 1992).

The extreme toxicity of dimethylmercury came to the attention of the scientific community most recently as the result of a tragic laboratory accident. In August 1996, Dr. Karen Wetterhahn, working at Dartmouth College, was exposed to approximately 400 milligrams of dimethylmercury when a few drops of a standard she was using to calibrate a nuclear magnetic resonance instrument accidentally spilled on the back of her latex glove. The spill occurred in a hood and she cleaned up the spill and removed the glove. Five months after the accident, she was admitted to the hospital exhibiting problems with her speech, balance, and gait. Twenty-two days after the onset of these neurological symptoms, she did not respond to visual or verbal stimuli, and lapsed into a coma. She died in June 1997, almost 300 days after the accident (Nierenberg *et al.*, 1998).

2.2 Study Design

2.2.1 Description

Mercury was chosen for inclusion in the LMMB Study as a representative of persistent, bioaccumulative metals. Mercury was measured in vapor, precipitation, particulates, atmospheric dry deposition, water in the open lake, tributaries, sediment, lower pelagic food web organisms, and top predator fish. The data generated from this study were used to estimate an overall mass balance of mercury in Lake Michigan (see Section 1.4). In addition, methylmercury was determined in tributary samples.

2.2.2 Scope

To develop a mass balance for mercury in Lake Michigan, all significant sources and stores of mercury in the environment were measured. Significant sources and stores included tributary inputs, atmospheric inputs from the vapor phase, particulate phase, and precipitation, sediment, lower pelagic food web organisms, and fish. The specific components that were studied are shown in Table 2-1.

Field sampling was conducted from February 1994 through October 1995, with an additional sampling cruise in May 1996 to retrieve sediment traps and collect samples at stations LM94-11, LM94-17, LM94-18, LM94-21S and LM94-32.

2.2.3 Organization/Management

The responsibility for collecting and analyzing mercury samples from the various components was divided among six principal investigators (PIs, see Table 2-1). Each principal investigator developed a quality assurance project plan (QAPP) that was submitted to EPA's Great Lakes National Program Office (GLNPO) for approval. The QAPPs detailed the project management, study design, and sampling and analysis procedures that would be used in the study and the quality control elements that would be implemented to protect the integrity of the data. The LMMB quality assurance program is further discussed in Section 2.6, and detailed information on the quality assurance activities and data quality assessment specific to each ecosystem component are discussed in Chapters 3 through 8.

Table 2-1. Components Sampled by Principal Investigators

Ecosystem Compartment	Component	Principal Investigator
Atmosphere	Vapor Particulate Precipitation	Gerald Keeler, Ph.D., University of Michigan School of Public Health Environmental Health Sciences
Tributary	Dissolved Mercury and Methylmercury Total Mercury and Methylmercury	James Hurley, Ph.D., University of Wisconsin Water Science and Engineering Laboratory
Open Lake	Particulate matter Total mercury	Robert Mason, Ph.D., University of Maryland Chesapeake Biological Laboratory
Sediment	Surficial sediment Resuspended sediment	Ronald Rossmann, Ph.D., USEPA Large Lakes Research Station
Lower Pelagic Food Web Organisms	Zooplankton Phytoplankton	Edward Nater, Ph.D., University of Minnesota Department of Soil, Water, and Climate
Fish	Lake Trout Coho Salmon	Jerome Nriagu, Ph.D., University of Michigan Department of Environmental Health Sciences School of Public Health

2.3 Sampling Locations

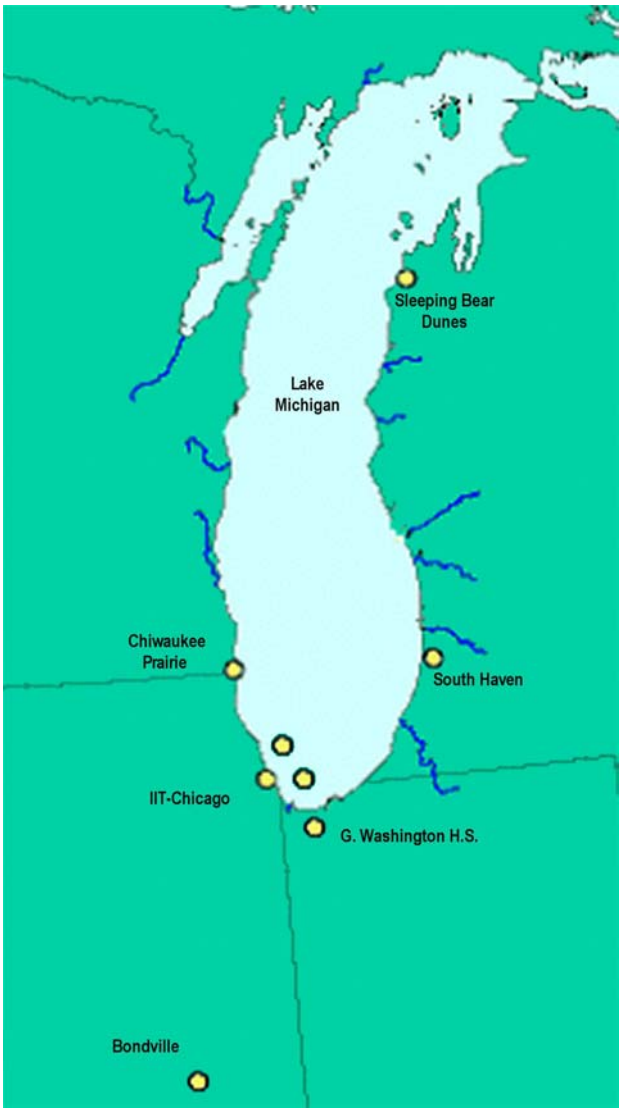
2.3.1 Atmospheric Components

Atmospheric samples were collected at five shoreline sampling stations and two open-lake sampling stations within Lake Michigan (Figure 2-2). One of the shoreline sampling stations (George Washington High School in Chicago) was used only once over the course of the study. In addition, one out-of-basin land-based sampling station was established as a regional background site to represent air coming over Lake Michigan during periods of southwest or northwest prevailing winds. The sampling locations and sampling frequencies for the LMMB Project were selected through discussions with experts in the field

during several workshops, including the Great Lakes Mass Balance Planning Workshop in April 1992 and the LMMB Planning Meeting in September 1993. Site-selection criteria considered predominant annual wind directions, source areas, and episodic summer events.

In general, sites were selected to be regionally representative of land-use categories and to represent the different potential sources of pollutants in this study (e.g., releases associated with population centers versus agricultural areas).

Figure 2-2. Atmospheric Sampling Stations



The shoreline atmospheric sampling stations include those specific to the LMMB Study as well as several that are part of the Integrated Atmospheric Deposition Network (IADN). Samples were collected from the land-based IADN stations at Sleeping Bear Dunes and Bondville from April 1994 through October 1995. Sampling at these IADN stations was governed by study design and quality assurance programs specific to IADN, but generally similar to those in the LMMB Study, so the data have been incorporated into the LMMB database. The locations of the shoreline atmospheric mercury sampling stations are shown in Figure 2-2.

Atmospheric samples were collected from the *R/V Lake Guardian* at two stations (Fig. 2-2) in the open lake in July 1994 and January 1995. However, because of the limited spatial and temporal coverage represented by these open-lake atmospheric samples, they were not included in the LMMB Study data set, nor are they discussed in this report.

For vapor and particulate samples, one 24-h composite sample was collected every 6 days using automated sampling equipment. Precipitation samples were collected by automated equipment that sensed the presence of precipitation and collected samples from each precipitation event during April through October. Precipitation samples collected in November through March were collected on a weekly basis (e.g., each sample represented the precipitation that fell during all of that week). These frequencies were generally followed as sampling schedules permitted and except in cases of sampler malfunction, lack of precipitation, or when circumstances prevented retrieval of a sample.

2.3.2 Tributaries

Tributary samples were collected from 11 rivers that flow into Lake Michigan (Figure 2-3). These tributaries included the Menoninee, Fox, Sheboygan, and Milwaukee Rivers in Wisconsin; the Grand Calumet River in Indiana; and the St. Joseph, Kalamazoo, Grand, Muskegon, Pere Marquette, and Manistique Rivers in Michigan. With the exception of the Pere Marquette River, these tributaries were selected for the LMMB Study because of elevated concentrations of contaminants in resident fish. The Pere Marquette River was selected because it has a fairly large and pristine watershed.

The 11 monitored tributaries represent greater than 90% of the total river flow into Lake Michigan and an even higher percentage of the total tributary load of pollutants into Lake Michigan. Samples collected from the Pere Marquette River can be used to estimate loads from the small portion of the Lake Michigan watershed that was not monitored in this study.

Table 2-2 describes specific watershed characteristics and impairment information for each of the monitored tributaries. Of the 11 tributaries, 6 (the Kalamazoo, Manistique, Menominee, Fox, Sheboygan, and Grand Calumet Rivers) are classified as Great Lakes areas of concern (AOCs). Areas of concern are severely degraded geographic areas within the Great Lakes Basin. They are defined by the US-Canada Great Lakes Water Quality Agreement (Annex 2 of the 1987 Protocol) as "geographic areas that fail to meet the general or specific objectives of the agreement where such failure has caused or is likely to cause impairment of beneficial use or the area's ability to support aquatic life." Most of the 11 tributaries are also listed on the Clean Water Act Section 303(d) list of impaired water bodies due to contamination from mercury, PCBs, and other pollutants.

Figure 2-3. Tributary Sampling Stations

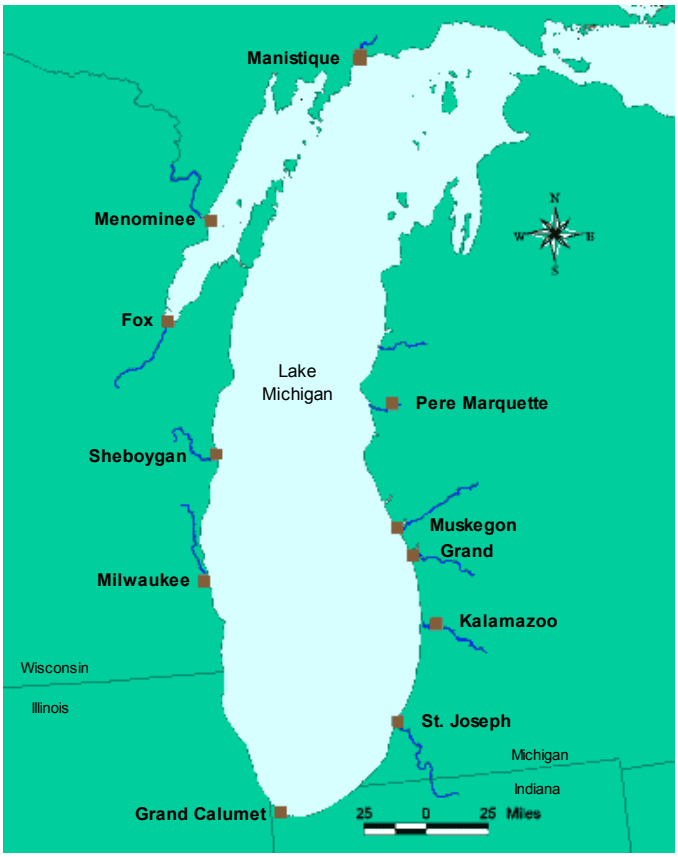


Table 2-2. Watershed Characteristics for Tributaries Monitored in the LMMB Study

Tributary	Watershed area (mi^2)	Total river miles in watershed	Riparian Habitat		IWI Score[a]	Impaired for[b]	Area of Concern
			Forested	Agricultural/ Urban			
St. Joseph	4685	3743	25-50%	>50%	3 - less serious problems, low vulnerability	*E. coli*, mercury, PCBs, pathogens, macro-invertebrate community	
Kalamazoo	2047	1560	25-50%	>50%	3 - less serious problems, low vulnerability	Mercury, PCBs	X
Grand (lower)	2003	2014	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs, pathogens	
Muskegon	2686	1886	25-50%	>50%	5 - more serious problems, low vulnerability		
Pere Marquette	2644	1356	25-50%	>50%	3 - less serious problems, low vulnerability	Mercury, PCBs	
Manistique	1464	1061	>75%	20-50%	1 - better quality, low vulnerability	Mercury, PCBs, pathogens	X
Menominee	2306	1660	>75%	20-50%	1 - better quality, low vulnerability	Dioxin, PCBs, mercury, pathogens	X
Fox (lower)	442	700	25-50%	>50%	6 - more serious problems, high vulnerability	PCBs, organic enrichment, dissolved oxygen	X
Sheboygan	2201	1699	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs, mercury	X
Milwaukee	864	802	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs	
Grand Calumet	1039	760	25-50%	>50%	5 - more serious problems, low vulnerability	PCBs, pesticides, lead, mercury, dissolved oxygen, cyanide, chlorides, impaired biotic community, oil and grease, copper	X

[a]EPA's Index of Watershed Indicators Score for assessing the health of aquatic resources.
[b]Based on 1998 listing of Clean Water Act Section 303(d) impaired waters.

2.3.3 Open Lake

Open-lake water column samples were collected from 17 sampling locations on Lake Michigan, one sampling location in Green Bay, and one sampling location on Lake Huron (Figure 2-4). Open-lake samples were collected during six cruises of the *R/V Lake Guardian* between June 1994 and September 1995. The dates of the six cruises are shown in Table 2-3.

Figure 2-4. Open-Lake Water Column Sampling Stations

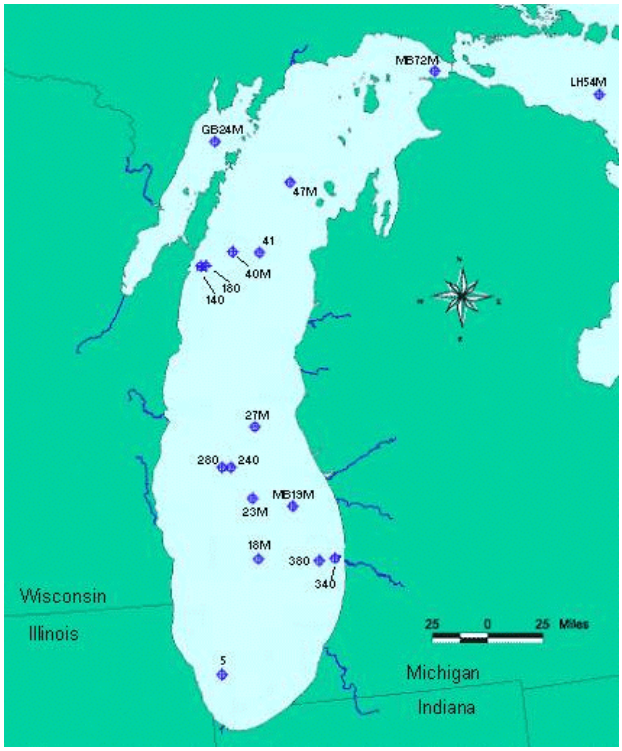


Table 2-3. Open-lake Cruise Dates

Cruise Date
June 1994
August 1994
October/November 1994
March/April 1995
August 1995
September/October 1995

The first cruise during which mercury samples were collected was in early summer (June 1994), after the onset of stratification. The second and third surveys were in late summer (August 1994) and fall (October 1994), during later stages of stratification. The fourth survey was conducted in March 1995, during non-stratified conditions. The fifth and sixth surveys occurred in August and September 1995, during stratification.

During stratification, samples were collected from two or three depths to represent the epilimnion and the hypolimnion. When the water column was unstratified, samples at some stations were collected from mid-depth, while at other stations, samples were collected from two depths.

2.3.4 Sediment

In 1994, 1995, and 1996, sediment samples were collected from Lake Michigan by box coring, Ponar grabs, and gravity coring. The location of the sediment sampling stations and the sampling device used are shown in Figure 2-5. The sediment sampling locations were selected to help define the three depositional zones (depositional, transitional, and non-depositional).

In addition to grab samples of sediments, sediment traps were deployed at eight locations in Lake Michigan (see Figure 2-6). The trap at Station 3, excluded from the figure but located in northern Lake Michigan, was lost. Samples from the two traps at Station 6 had mercury chloride added as a preservative to their collection bottles prior to deployment and therefore were not analyzed. The trap placed at a depth of 245 m at Station 5 failed, and no sample was available from the trap at Station 4. Enough sample was available for mercury analysis from Stations 1, 2, 5, 7, and 8. Samples from two depths were available from Stations 7 and 8.

Figure 2-5. Locations of Sediment Cores

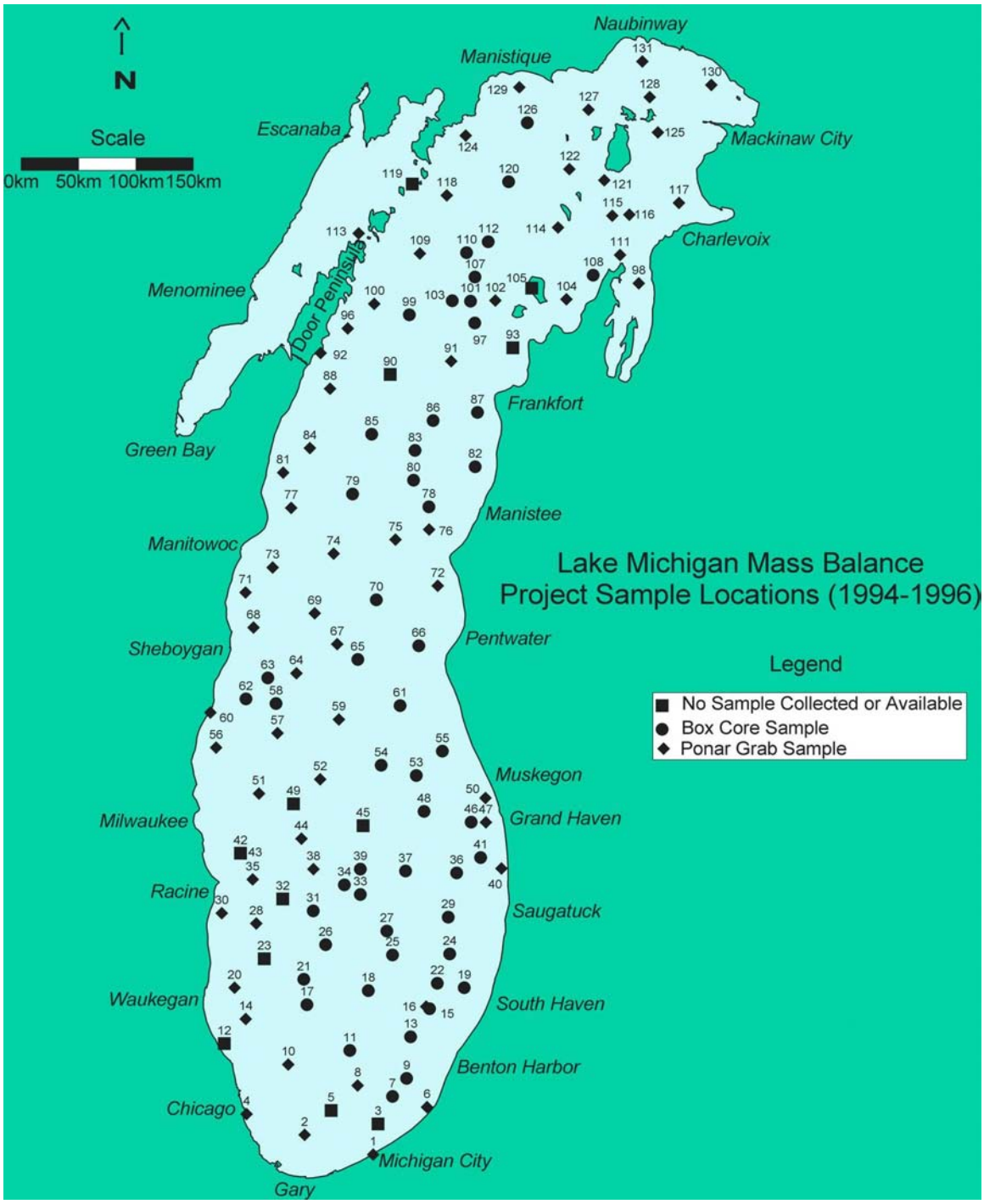
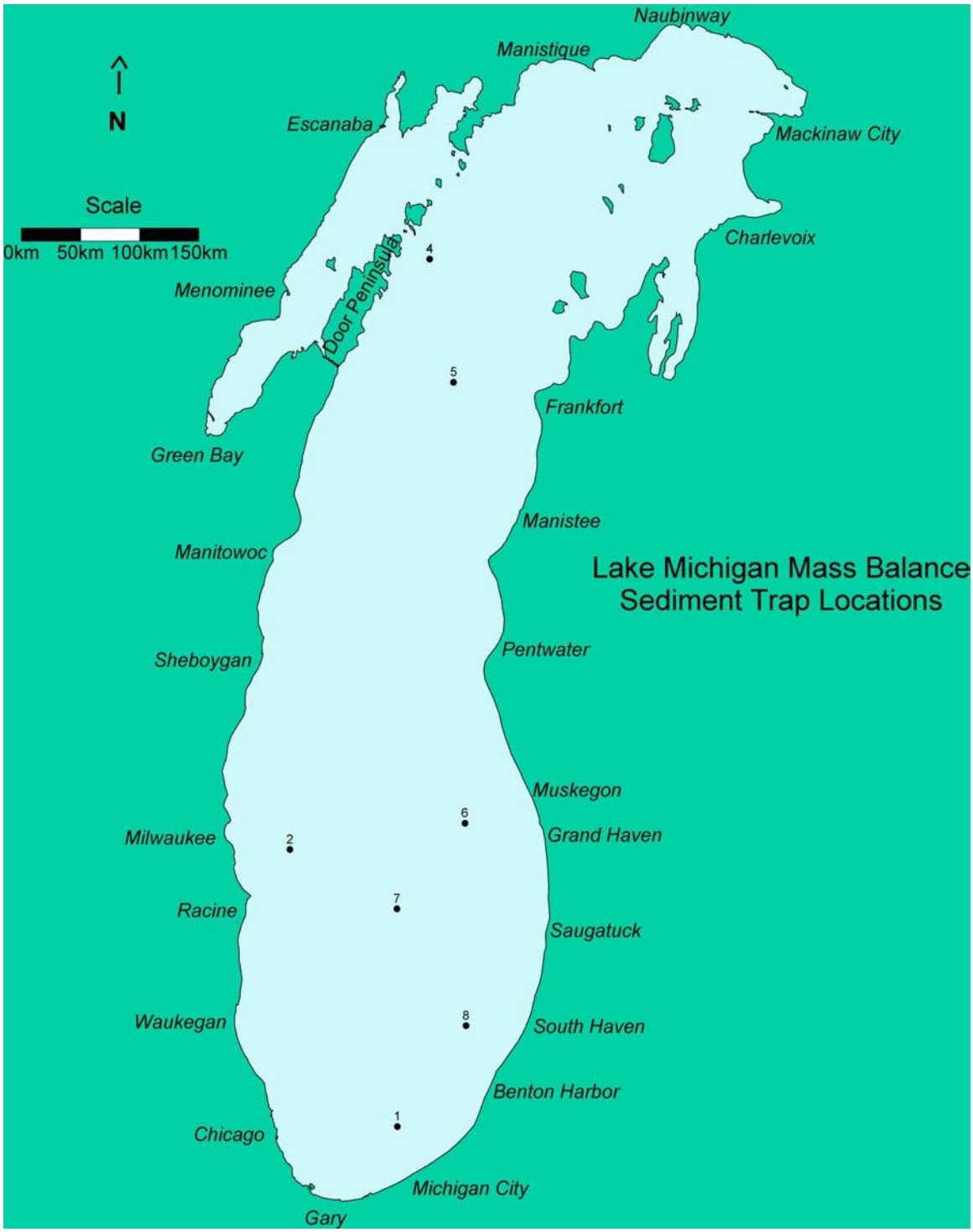


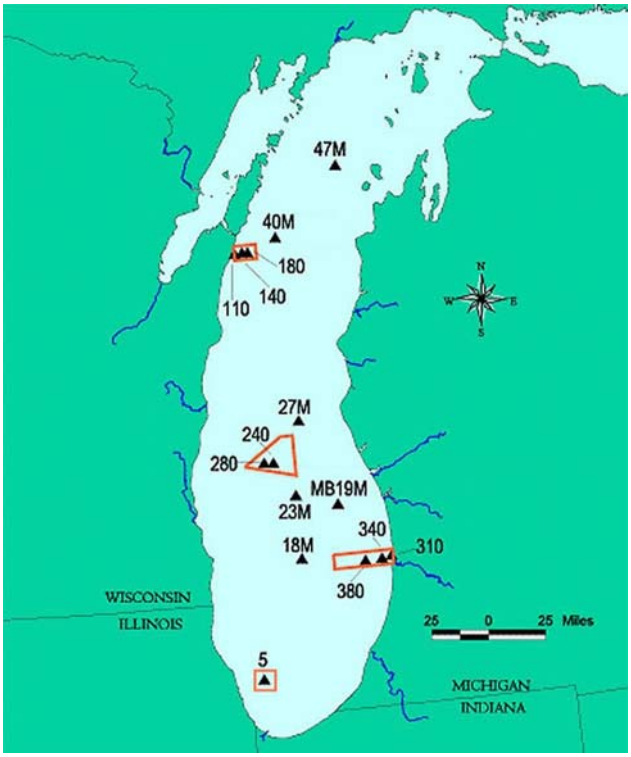
Figure 2-6. Sediment Trap Locations



2.3.5 Lower Pelagic Food Web Organisms

Plankton samples were collected from 12 stations in Lake Michigan selected by GLNPO and the PIs in advance of sampling (Figure 2-7). The stations included eight stations in three biological sampling areas or "biota boxes" (Stations 110, 140, 180, 240, 280, 310, 340, and 380), three master stations (18M, 27M, and 47M), and a fourth biota box centered around Station 5, near Chicago. The four biota boxes are outlined in red in Figure 2-7. Samples were collected on several occasions, from June 1994 to September 1995.

Figure 2-7. Sampling Stations for Lower Pelagic Food Web Organisms and Fish



In addition, zooplankton samples were collected from Station 10M in January 1995 and phytoplankton samples were collected from Stations 23M and 41 in June 1994. A total of 72 zooplankton and 71 phytoplankton samples were collected during the study.

2.3.6 Fish

Lake Michigan fish were collected from April 1994 through October 1995 for total mercury analysis. Lake trout and coho salmon were collected using gill nets, trawl nets, or other appropriate means (Table 2-4). Up to five individual fish of the same species and size or age category were combined to produce composite fish samples at each collection. In total, 693 adult lake trout from 172 to 933 mm in length were collected from three of the four biological sampling areas or biota boxes shown in Figure 2-7 (fish were *not* collected from the biota box at Station 5, near Chicago):

- **Sturgeon Bay biota box** — a series of three nearshore stations (110, 140, and 180) on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** — a series of two mid-lake reef stations (240 and 280) in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** — a series of three nearshore stations (310, 340, and 380) on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan

Table 2-4. Number of Fish Collected by Technique

Species	Number of Fish Collected by Technique				
	Hook and Line	Gill Net	Bottom Trawl	Harvest Weir	Dip Net
Lake Trout	—	666	27	—	—
Coho salmon — adult	135	3	—	—	—
Coho salmon — yearling	29	—	—	9	—
Coho salmon — hatchery	—	—	—	—	25

These fish were used to prepare 156 trout composite samples that were analyzed for total mercury by cold vapor atomic fluorescence spectroscopy (Table 2-5).

A total of 201 coho salmon were collected in three distinct age classes (hatchery, yearlings, and adult). Of the 201 fish, 138 were adult coho salmon collected from 54 sites selected to follow the seasonal migration of coho, which travel up Lake Michigan tributaries in the fall to spawn. During the summer, coho salmon were collected from the east central and west central regions of the lake. During the fall, coho salmon were collected from the northeastern side of the lake near the Platte River and on the western side of the lake near the Kewaunee River. These 138 adult coho salmon were used to prepare 32 composite samples for mercury analyses (Table 2-5). In addition, 38 yearling coho salmon were collected from 22 locations to create 8 composite samples, and 25 young (hatchery) coho salmon were collected directly from the Platte River hatchery, where the majority of Lake Michigan stocked salmon originate, and were used to create 5 composite samples.

Table 2-5. Number of Fish Collected by Species and Location

Species	Total Number of Individual Fish Collected	Number of Locations	Number of Composite Samples Created
Lake Trout	693	3	156
Coho salmon — adult	138	54	32
Coho salmon — yearling	38	22	8
Coho salmon — hatchery	25	1	5

2.4 Sampling Methods

Full details of the sampling methods used in the LMMB Study have been published by EPA in a methods compendium (USEPA, 1997d and 1997e). Field sampling for all media except sediment and fish adhered to strict protocols for the sampling of trace metals using "clean" techniques. Sampling personnel were outfitted with suits and gloves, "clean hands/dirty hands" techniques were employed, and pre-cleaned polytetrafluoroethylene bottles and equipment were used. "Clean" techniques were not used for the collection of sediments or fish, because these matrices were believed to contain significantly higher mercury concentrations, so contamination from background sources would be less of a concern. Brief summaries of the sampling procedures are provided below.

2.4.1 Atmospheric Components

2.4.1.1 Vapor Fraction

Vapor-phase mercury was quantitatively removed from air by amalgamation onto gold. Two gold-coated borosilicate glass bead traps in quartz tubing (with glass fiber pre-filters) were used in series. The traps were housed in a sampling box 3 m above the ground and maintained at 93 °C to prevent condensation. Samples were collected for 12-24 hours at flow rates of 10 to 30 L/min.

2.4.1.2 Particulate Fraction

Particulate atmospheric components were collected using a filter pack assembly containing pre-treated 47-mm glass fiber filters housed in custom-made sampling boxes. The volume of air sampled was measured with a calibrated dry test meter. The vacuum pumps attached to the sampling boxes were specially designed for trace level mercury sampling. The apparatus was deployed 3 m above the ground, and samples were collected for 12-24 hours at flow rates of 10 to 30 L/min.

2.4.1.3 Precipitation Fraction

Precipitation samples were collected by automated equipment that sensed the presence of precipitation and collected samples from each precipitation event during July 1994 to October 1994, and during each precipitation event from April 1995 to October 1995. Precipitation samples collected from November 1994 through March 1995 were collected on a weekly basis (e.g., each sample represented the precipitation that fell during all of that week). An automated sensor grid on the modified collector was activated by precipitation, causing the lid of the sampler to open for wet-only collection of precipitation samples. Samples were collected through a borosilicate funnel and in 1-L Teflon® bottles.

2.4.2 Tributaries

A small boat was anchored at the sampling site, above the centroid of the river. Water samples (500 mL) were collected from two depths (0.2 x river depth and 0.8 x river depth). Water was pumped through a Teflon® sampling tube (weighted with a Teflon® weight) and C-flex® pumphead tubing using a peristaltic pump. Dissolved samples were collected using in-line filtration. Mercury samples were preserved in the field with 10 mL of 50% HCl. Samples from the upper and lower depths were composited.

2.4.3 Open Lake

Open-lake samples were collected from various depths depending upon the stratification conditions. During stratification, open-lake stations were sampled at the mid-epilimnion and mid-hypolimnion. During non-stratified periods, samples were collected at mid-water column depth and two meters below the surface. Master stations, during times of non-stratification, were sampled at mid water column, one meter below the surface, and two meters off the bottom. During times of stratification, master stations were sampled at one meter below the surface, mid-epilimnion, mid-hypolimnion, and two meters off the bottom.

Teflon®-lined Go-Flo bottles were attached to Kevlar® lines with non-metallic weights. Two liters of sample were collected for total mercury analysis. Samples were aliquotted and filtered in a clean room onboard the ship. Particulate samples were collected onto 0.8-µm quartz fiber filters. Samples were frozen on board and shipped overnight to the laboratory.

2.4.4 Sediment

Sediment samples were collected from 118 stations in Lake Michigan using two types of equipment (Figure 2-5). Wherever sediments were sufficiently soft and fine grained to permit safe use of the box corer, the box corer was preferred for sampling. After retrieval of the box core, four subcores were taken from each box core. The subcore designated for radionuclide and mercury analyses was subsectioned at 1-cm intervals from top to bottom. The surficial 1 cm of each of these cores was analyzed for mercury. Box cores were collected from 51 stations during the study.

The second, and less preferred, method of collection was grab sampling using a Ponar sampler. Many sandy or stiff lake clay regions of sediment within the lake could not be box cored, so Ponar samples were collected at these locations. When retrieved, the Ponar was carefully drained and opened. The surficial 1-cm sediment layer was removed from the grab sample. If the surficial sediment layer contained less than 1 cm of recent sediment, then only the recent sediment was sampled. Recent sediment was visually identifiable from older sediments by changes in cohesiveness, color, and grain size. Older sediments were generally cohesive red-brown clays, whereas, recent sediments were brown to gray non-cohesive silty and clayey sands. In most instances, there was at least 1 cm of recent sediment. This surficial 1-cm layer was analyzed for mercury. Ponar samples were collected from 67 stations during the study.

Sediment traps were deployed at eight locations (Figure 2-6). The trap at Station 3, located in northern Lake Michigan (excluded from Fig. 2-6), was lost. Samples from the two traps at Station 6 had mercury chloride added as a preservative to their collection bottles prior to deployment and therefore were not analyzed. The trap at 245 m deep at Station 5 failed, and no sample was available from the trap at Station 4. Enough sample was available for mercury analysis from Stations 1, 2, 5, 7, and 8. Samples from two depths were available from Stations 7 and 8. Details of trap sampling can be found in Eadie (1997a, 1997b). All samples and subsamples collected were placed in polyethylene bags or bottles, immediately frozen on board the ship, and transported frozen to laboratory freezers (Edgington and Robbins 1997a).

2.4.5 Lower Pelagic Food Web Organisms

Phytoplankton were collected using a device called a phytovibe. This device was specially designed and constructed for GLNPO for collecting large volumes of plankton for analysis of chemical contaminants such as mercury and PCBs. The phytovibe consists of a pair of inverted pyramids constructed of stainless steel mesh lined with 10-µm Nitex netting. Water is pumped by a submersible pump through nylon tubing into the top of the device, which has an opening that is 1 m^2. The end of the nylon tubing is covered with 100-µm netting to remove zooplankton. In order to prevent plugging of the netting with plankton, the phytovibe is shaken by a motor. The samples were washed down into a detachable sampling cup with lake water and collected for processing. Sampling times ranged from 6 to 14 hours, depending on plankton concentration in the water and sample size needed for a particular analysis.

The depth of collection was chosen based on interpretations of the temperature, fluorescence, and turbidity profiles from the ship, with the objective of choosing a depth that maximized the occurrence of phytoplankton that were being grazed. This generally corresponded to the epilimnion or the subthermocline chlorophyll maximum in stratified conditions.

Zooplankton were collected in nested Nitex nets of two different mesh sizes (102-µm and 500-µm) during standard vertical tows, from near the bottom to the surface. The 500-µm nets were used to exclude larger organisms, including small fish, from the zooplankton samples. The number of tows performed was dependent on the mass of sample collected per tow. The required wet weight of material for mercury analyses was usually obtained in one or two tows.

2.4.6 Fish

Whole fish were collected intact, with all body fluids and no incisions, except lake trout, which had their stomachs removed. Fish were wrapped in aluminum foil, placed in polyethylene bags, tagged, and frozen onboard the vessel. The fish were aged by checking for coded wire tags on the head and for fin clips. Whole fish were then composited by age, location, species, and size range. Samples were homogenized using a 40-quart vertical cutter mixer for large fish, a 12-quart vertical cutter for medium sized fish, or a high-speed 2-quart cutter for small fish.

2.5 Analytical Methods

Full details of the analytical methods used in the LMMB Study have been published by EPA in a methods compendium (USEPA, 1997d and 1997e). Brief summaries of the specifics of the analyses for each lake component are provided in Sections 2.5.1 to 2.5.6. Except for the analyses of sediment samples, all of the other media used cold vapor atomic fluorescence spectrometry (CVAFS) instrumentation and sample preparation and analysis procedures that were similar to those described in EPA Method 1631 and Bloom and Fitzgerald (1988). The sediment sample analyses were conducted using cold vapor atomic absorption (CVAA) instrumentation.

2.5.1 Atmospheric Components

2.5.1.1 Vapor Fraction

The mercury collected on gold-coated glass beads was thermally desorbed from the traps at 500 °C and carried into a CVAFS analyzer.

2.5.1.2 Particulate Fraction

The glass fiber filters used to collect particulate atmospheric mercury were digested in 1.6 M nitric acid, using a microwave digestion procedure to release the mercury from the particulate material. The mercury in the digestate was then determined by oxidation with bromine monochloride, purge and trap, and CVAFS.

2.5.1.3 Precipitation Fraction

The mercury in precipitation samples was determined by oxidation with bromine monochloride, purge and trap, and CVAFS, without digestion.

2.5.2 Tributaries

Water samples from the tributaries were analyzed for mercury using the analytical techniques outlined in EPA Method 1631. Briefly, the mercury in a 100-mL sample aliquot was oxidized to Hg^{+2} with bromine monochloride. The sample was reduced with $NH_2OH{\cdot}HCl$ to destroy the free halogens, then reduced with stannous chloride ($SnCl_2$) to convert dissolved Hg^{+2} to volatile Hg^0. The Hg^0 was separated from solution by purging with an inert gas, collected onto a gold trap, and thermally desorbed from the trap into an inert gas stream that carried the Hg^0 into the cell of a CVAFS analyzer for detection.

Water samples were analyzed for methylmercury using a combination of distillation, ethylation, gas chromatography, and cold-vapor atomic fluorescence spectrometry. Briefly, methylmercury was distilled from a water sample with heat and a flow of inert gas. The distillate was treated with sodium tetraethyl borate, which converts the methylmercury to the more volatile methylethylmercury, which was separated on a gas chromatographic column. The methylethylmercury was pyrolyzed and converted to Hg^0, and swept into the CVAFS analyzer for determination of mercury.

2.5.3 Open Lake Water

Water samples from the open lake were analyzed for mercury using the same techniques described above for tributary samples.

2.5.4 Sediment

Sediment samples were freeze-dried in the laboratory in pre-weighed storage containers. The freeze-dried samples were stored in these containers until subsamples were removed for analysis. Samples were digested in one of two ways. Most surficial sediments were digested using a Leeman Labs, Inc., automated mercury system. The sediment trap samples and a few surficial sediment samples were digested using a 1.6 M nitric acid solution and a microwave digestion system (Uscinowicz and Rossmann 1997). The Leeman automated digestion uses 50% aqua regia and potassium permanganate solutions and provides a more vigorous digestion than the microwave procedure.

All samples were analyzed using a Leeman Labs, Inc. automated mercury analysis system. The analysis is based upon the cold vapor atomic absorption spectrophotometry (CVAAS) technique that reduces divalent mercury in solution to elemental mercury vapor using stannous chloride. Argon is used to carry the elemental mercury to the detector (Uscinowicz and Rossmann 1997).

2.5.5 Lower Pelagic Food Web Organisms

Freeze-dried plankton samples were placed in a PFA Teflon® digestion vessel with a 1:1 concentrated sulfuric acid and nitric acid mixture, then placed in a 70 °C hot water bath overnight. Mercury was determined by oxidation with bromine monochloride, purge and trap, and CVAFS.

2.5.6 Fish

Samples were digested in concentrated nitric acid by microwave digestion under high pressure and temperature. Mercury analysis was performed using CVAFS.

2.6 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The goal of the QA program was to ensure that all data gathered during the LMMB Study met defined standards of quality with specified levels of confidence. Data quality was defined, controlled, and assessed through activities that included development of study QAPPs, use of SOPs, and data verification. These activities are described in detail in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). Specific quality control elements implemented in the sampling and analysis of mercury included:

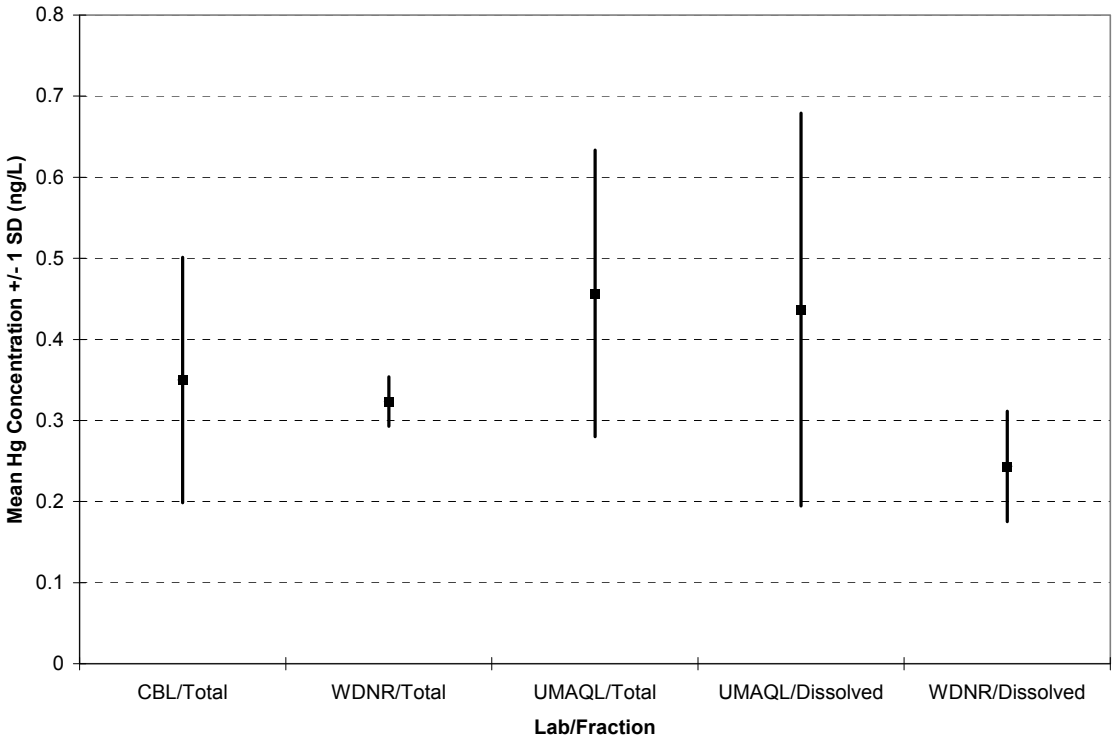
- use of standard operating procedures and trained personnel for field sampling and laboratory analysis;
- determination of method sensitivity through calculation of method detection limits;
- preparation and analysis of a variety of blanks to characterize contamination associated with specific sample handling, storage, and analysis processes including field blanks, lab reagent blanks, bottle blanks, trip blanks, and lab procedural blanks;
- collection and analysis of field or laboratory duplicate samples;
- analysis of standard reference materials;
- preparation and analysis of a variety of quality control samples including performance standards;
- use of a standardized data reporting format; and
- preparation and analysis of matrix spike samples to characterize the applicability of the analytical method to the study sample matrices.

In September 1995, GLNPO conducted an intercomparison study involving the mercury PIs at the Chesapeake Biological Laboratory (CBL), the University of Wisconsin Department of Natural Resources (WDNR), and the University of Michigan Air Quality Laboratory (UMAQL). The performance of these three laboratories could be more readily compared because they were analyzing similar sample matrices, e.g., river water, lake water, and precipitation. The performance of the laboratories analyzing the plankton, fish, and sediment samples could not be compared in a similar fashion, given the significant differences in the sample preparation procedures used for each of these matrices. The study compared the submersible pump collection technique performed by Gerald Keeler (University of Michigan) and the Go-Flo bottle technique performed by Robert Mason (University of Maryland's Chesapeake Biological Laboratory). Drs. Keeler and Mason collected samples from the same point aboard the *R/V Lake Guardian*. Dr. Hurley collected samples from an inflatable boat rowed several hundred yards from *R/V*

Lake Guardian. Each of the PIs analyzed the samples in triplicate using the cold vapor atomic fluorescence techniques described in Section 2.5.

The results are shown in Figure 2-8. The laboratory and sample fraction (total mercury vs. dissolved mercury) are shown on the x-axis. The vertical bars represent the mean mercury concentration ± one standard deviation for each laboratory/fraction combination. The Chesapeake Biological Laboratory only provided data for total mercury. The mean total mercury concentrations from all three laboratories agree within a factor of 1.4. The mean dissolved mercury concentrations from the two laboratories that submitted dissolved mercury data agree within a factor of 1.8.

Figure 2-8. Results from Intercomparison Study of Three LMMB Laboratories Analyzing Mercury in Aqueous Samples



In addition to the intercomparison study, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data. Prior to data submission, each researcher submitted electronic test files containing field and analytical data according to the LMMB data reporting standard. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers.

Prior to sample collection, quality assurance project plans (QAPPs) were developed by the PIs and submitted to GLNPO for review. In the QAPPs, the PIs defined measurement quality objectives (MQOs) in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. The MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs. The MQOs for mercury are listed in Section 5 of *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

The PI-defined MQOs also were used in the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for verifying the quality of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If the results failed to meet MQOs and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. In addition, a wide variety of flags were applied to the data to provide detailed information to data users. For example, the flag LAC (laboratory accident, no result reported) was applied to sample results to document that a sample was collected, but no result was reported due to a laboratory accident. The frequencies of flags applied to mercury study data are provided in the Quality Implementation Sections of each of the following chapters. The flag summaries include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information (such as LAC). In order to provide detailed quality information to data users, the study data are maintained in the GLENDA database with all applied flags. Detailed definitions of the flags can be found in the Allowable Codes Table on GLNPO's website at: www.epa.gov/glnpo under Result Remark, List of QC flags (lab_rmrk).

The PIs participating in the study also conducted real-time data verification. PIs applied best professional judgement during sampling, analysis, and data generation, based on their experience monitoring mercury in the environment. In most cases, when sample results were questionable, the PI reanalyzed the sample or clearly documented the data quality issues in the database through the application of data quality flags or by including comments in the database field, "Exception to Method, Analytical." Because the flags and comments are maintained in the database for each sample result, data users are fully informed of data quality and can evaluate quality issues based on their intended use of the data. The level of documentation that GLNPO is maintaining in the study database is unprecedented for a database of this size and will serve as a model for future efforts.

GLNPO also conducted data quality assessments in terms of three of the six attributes used as the basis for the MQOs, specifically sensitivity, precision, and bias. For example, system precision was estimated as the mean relative percent difference (RPD) between results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between results for laboratory duplicate pairs. Bias was estimated using the mean recovery of spiked field samples or other samples of known concentration such as laboratory performance standards. A summary of data quality assessments is provided for the mercury study data in the Quality Implementation Section of each of the following chapters.

Chapter 3
Mercury in Atmospheric Components

3.1 Results

From June 11, 1994 to October 30, 1995, atmospheric samples were collected from five shoreline sampling station and one out-of-basin sampling station (Table 3-1 and Figure 2-2 in Chapter 2). Atmospheric samples were collected from three separate sampling media or phases: vapor (ng/m^3), particulate (pg/m^3) and precipitation (ng/L). A total of 387 vapor phase samples, 399 particulate phase samples, and 407 precipitation phase samples were collected and analyzed for total mercury.

Table 3-1. Numbers of Atmospheric Samples Analyzed for Mercury

Sampling Station		Sampling Dates	Number of Vapor Samples Analyzed	Number of Particulate Samples Analyzed	Number of Precipitation Samples Analyzed	Total Samples Analyzed
Shoreline Atmospheric Sampling Stations	Chiwaukee Prairie	7/19/94 to 10/30/95	73	79	74	226
	George Washington H.S.	7/19/94 to 7/25/94	1	2	0	3
	IIT Chicago	6/11/94 to 10/30/95	80	83	74	237
	Sleeping Bear Dunes	6/23/94 to 10/30/95	80[1]	80	97	257
	South Haven	6/19/94 to 10/30/95	79	81	81	241
Out-of-basin Atmospheric Sampling Stations	Bondville	6/24/94 to 10/30/95	74	74	81	229
Total			387	399	407	1193

[1] One sample was invalid.

3.1.1 Vapor Fraction

Between 73 and 80 vapor-phase samples were collected from four shoreline atmospheric stations and one out-of-basin station (Bondville, located in Illinois). In addition, one sample was collected at George Washington High School. Because of the representativeness issues with using a single sample, this result was not used in any of the analyses. The overall mean vapor-phase concentration was 2.44 ng/m^3.

Table 3-2. Mean Mercury Concentrations Measured in the Vapor Phase

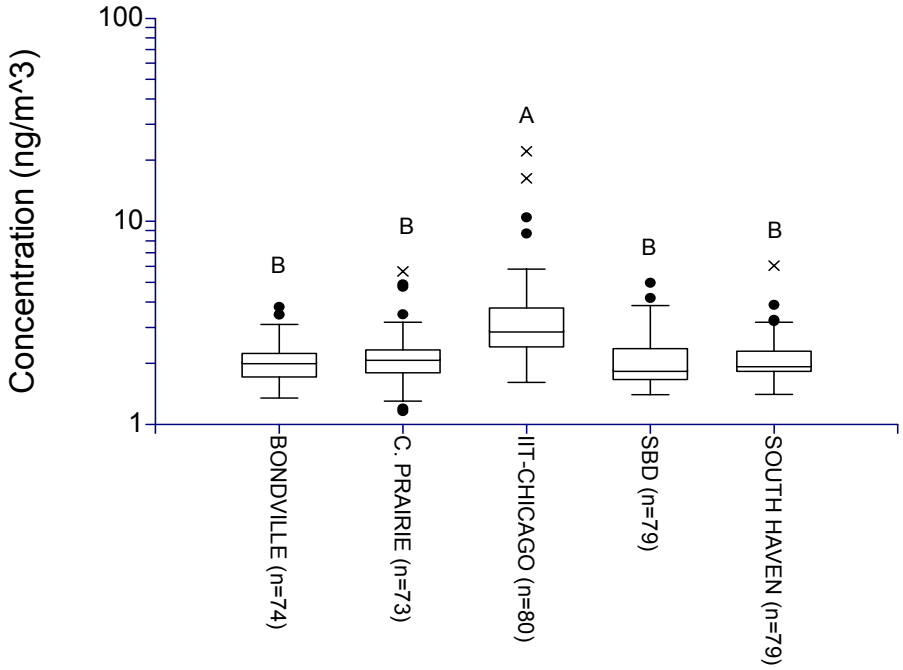
Sampling Station	N	Mean (ng/m^3)	Median (ng/m^3)	Range (ng/m^3)	SD (ng/m^3)	RSD (%)	Below DL (%)
Chiwaukee Prairie	73	2.20	2.10	1.16 to 5.68	0.740	33.6	0
George Washington H.S.	1	2.31	2.31	NA	NA	NA	0
IIT Chicago	80	3.62	2.90	1.61 to 22.2	2.89	80.0	0
Sleeping Bear Dunes	79	2.12	1.86	1.40 to 4.99	0.694	32.8	0
South Haven	79	2.16	1.96	1.41 to 6.05	0.647	29.9	0
Bondville	74	2.06	2.03	1.35 to 3.80	0.469	22.7	0

NA = Not applicable

3.1.1.1 Geographical Variation

Mean vapor-phase mercury concentrations ranged from 2.06 ng/m^3 at Bondville to 3.62 ng/m^3 at IIT Chicago (Table 3-2). The mean concentration at IIT Chicago was significantly greater than those of the other stations, based on an analysis of variance (ANOVA) model with the Tukey method for pairwise comparisons (results log-transformed prior to analysis). This was to be expected, because this station was the only one classified as an urban sampling location. Among the remaining stations, only Chiwaukee Prairie was located within 10 km of an urban area. The maximum concentration of 22.2 ng/m^3 observed at IIT Chicago was more than three times greater than the highest concentration observed at any of the other stations (6.05 ng/m^3 at South Haven). The differences in mercury concentrations at the five stations are shown in Figure 3-1.

Figure 3-1. Mercury Concentrations in Atmospheric Vapor Measured at Four Lake Michigan Shoreline Sites and One Out-of Basin Site (Bondville)

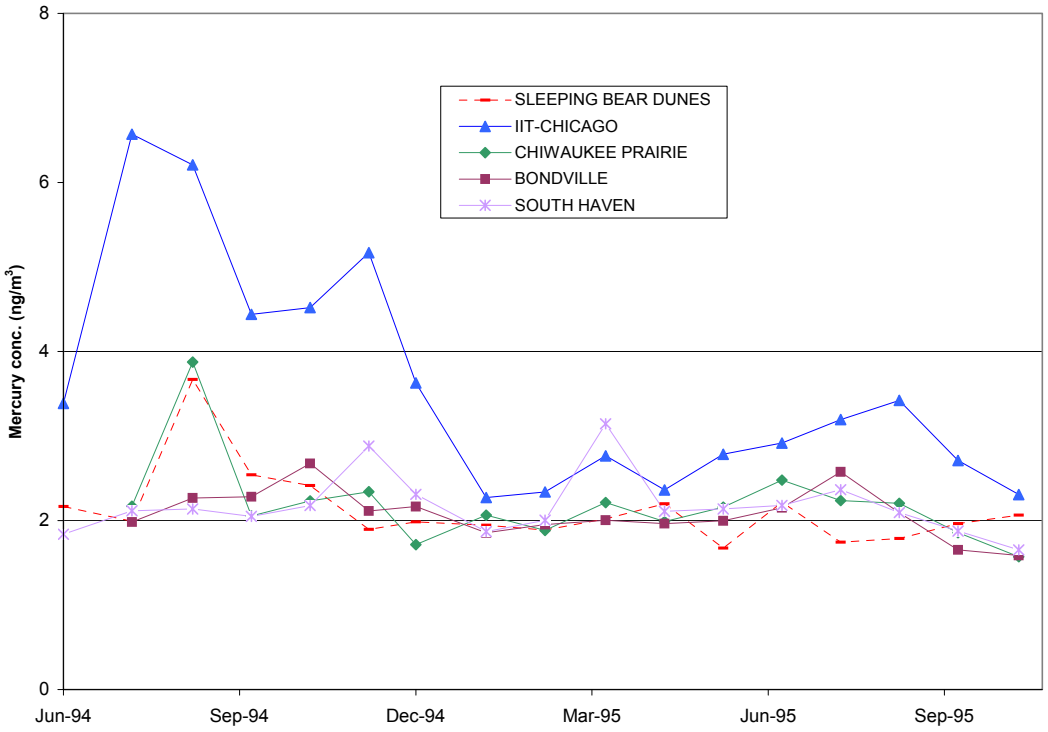


Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). The George Washington High School sampling site was not included in the analysis of variance due to the small number of samples. C. Prairie = Chiwaukee Prairie, SBD=Sleeping Bear Dunes

3.1.1.2 Seasonal Variation

Beginning in July 1994, samples were collected approximately weekly at each station. Therefore, there were multiple results from each station for each month in this interval, as well as one to two results during June 1994 at three of the stations. A time plot of the monthly mean concentrations from each station is presented in Figure 3-2.

Figure 3-2. Arithmetic Monthly Means at each Station - Vapor Phase



At IIT Chicago, there appears to be a difference in concentrations between the years 1994 and 1995. With the exception of June 1994, for which only 2 samples were collected, the monthly means from 1994 are greater than any of the monthly means for 1995. Based on a two-sample *t*-test using Satterthwaite's correction for differences in variability, this annual difference is significant ($p<0.0001$; using individual log-transformed results). Annual differences are less noticeable for the other stations, however, the means were significantly greater in 1994 for Bondville ($p=0.0328$) and Sleeping Bear Dunes ($p=0.0058$). These differences may have been due to seasonality rather than annual shifts, as most samples collected in the winter were collected in 1995.

Peaks occurred at IIT Chicago during July and August 1994, November 1994, and August 1995. Many of the other stations also had peaks during summer months. For example, the maximum monthly means for Sleeping Bear Dunes and Chiwaukee Prairie occurred during August 1994. At Bondville, the maximum mean occurred during October 1994. At South Haven the maximum concentration occurred in March 1995, and in fact exceeded the mean at IIT Chicago during that month. After classifying individual sample results according to season based on the collection date, significant differences between seasons occurred at IIT Chicago ($p=0.0014$) and Chiwaukee Prairie ($p=0.0228$), but not the other stations, based on a one-way ANOVA model, with results log-transformed prior to analysis. At IIT Chicago, the mean concentration during summer was significantly greater than the means of sample concentrations collected during spring and winter, based on the Tukey method for pairwise comparisons. At Chiwaukee Prairie, the mean concentration of samples collected during summer was significantly greater than the mean concentration during autumn.

3.1.2 Particulate Fraction

Between 74 and 83 particulate-phase samples were collected from four shoreline atmospheric stations and one out-of-basin station (Bondville). In addition, two samples were collected at George Washington High School. Because of the representativeness issues with using only two samples, these results were not used in any of the analyses. The overall mean particulate-phase concentration was 30.7 pg/m^3.

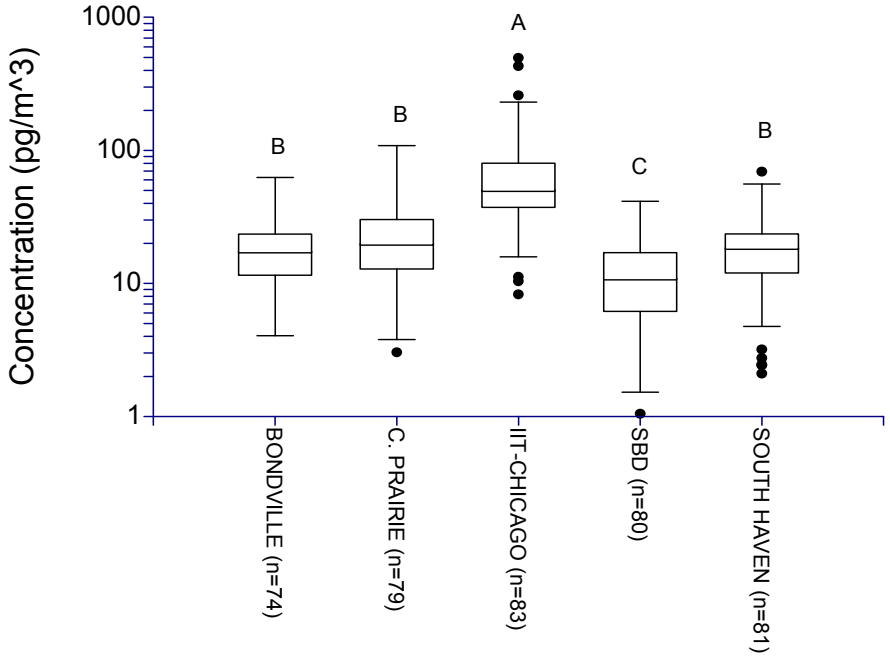
Table 3-3. Mean Mercury Concentrations Measured in the Particulate Phase

Sampling Station	N	Mean (pg/m^3)	Median (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	Below DL (%)
Chiwaukee Prairie	79	24.0	19.9	3.03 to 108	18.2	75.6	0
George Washington H.S.	2	151	151	58.6 to 244	131	86.7	0
IIT Chicago	83	73.7	50.4	8.25 to 494	77.2	105	0
Sleeping Bear Dunes	80	12.1	10.9	1.05 to 41.3	8.28	68.2	0
South Haven	81	19.3	18.5	2.10 to 69.0	12.2	63.1	0
Bondville	74	18.7	17.4	4.04 to 62.5	11.0	58.8	0

3.1.2.1 Geographical Variation

Mean particulate-phase mercury concentrations ranged from 12.1 pg/m^3 at Sleeping Bear Dunes to 73.7 pg/m^3 at IIT Chicago (Table 3-3). The mean concentration at IIT Chicago was greater than the maximum concentrations at all stations other than Chiwaukee Prairie. Based on an ANOVA model with the Tukey method for pairwise comparisons, the mean concentration at IIT Chicago was significantly greater than those of the other stations and the mean concentration at Sleeping Bear Dunes was significantly lower than those of the other stations (results log-transformed prior to analysis). These differences are not unexpected, given the locations of the different stations. In addition to IIT Chicago being the only station located in an urban area, Sleeping Bear Dunes is the only station located more than 50 km from an urban area. The differences in mercury concentrations at the five stations are shown in Figure 3-3.

Figure 3-3. Mercury Concentrations in Atmospheric Particles Measured at Five Lake Michigan Shoreline Sites and One Out-of Basin Site (Bondville)



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). The George Washington High School sampling site was not included in the analysis of variance due to the small number of samples.
C. Prairie = Chiwaukee Prairie, SBD = Sleeping Bear Dunes

3.1.2.2 Seasonal Variation

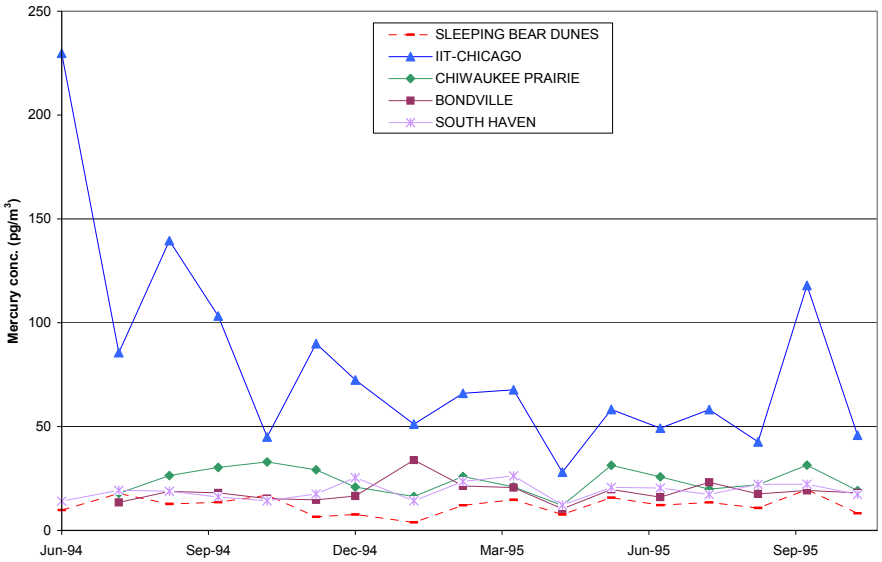
Beginning in July 1994, samples were collected approximately weekly at each station. Therefore, there were multiple results from each station for each month in this interval, as well as one to two results during June 1994 at three of the stations. A time plot of the monthly mean concentrations from each station is presented in Figure 3-4.

Particulate sample concentrations from IIT Chicago seem to exhibit the same annual difference observed in vapor samples, although to a lesser extent. Three of the four highest concentrations at IIT Chicago occurred during 1994. However, it is worth noting that the June 1994 maximum was based on only two samples and is therefore more variable than the other monthly means, which were based on at least four samples. The difference between years was significant for IIT Chicago ($p=0.0456$), but not for the other stations, based on a two-sample *t*-test run on the individual log-transformed results, with Satterthwaite's correction for differences in variance.

Other than IIT Chicago, the stations did not exhibit much variability between months and there was little evidence of any effects of seasonality. There was some consistency between these stations during May 1995, when all stations had relative minimum concentrations, and in September 1995, when all stations had relative maximum concentrations. Mercury concentrations differed significantly between seasons

only at Sleeping Bear Dunes (p=0.0311), based on a one-way ANOVA model with the Tukey method for pairwise comparisons (results log-transformed prior to analysis). For this station, the mean concentration of samples collected in summer was significantly greater than the mean concentration in winter.

Figure 3-4. Arithmetic Monthly Means at each Station - Particulate Phase



3.1.3 Precipitation Fraction

Between 74 and 97 precipitation-phase samples were collected from four shoreline atmospheric stations and one out-of-basin station (Bondville, located in Illinois). The overall mean precipitation-phase concentration was 20.6 ng/L.

Table 3-4. Mean Mercury Concentrations by Station Measured in the Precipitation Phase

Sampling Station	N	Mean (ng/L)	Volume-weighted Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Chiwaukee Prairie	74	23.1	16.5	19.9	4.47 to 134	18.3	79.1	0
IIT Chicago	74	26.1	21.1	20.4	5.45 to 74.6	15.5	59.5	0
Sleeping Bear Dunes	97	15.2	11.0	11.0	2.09 to 63.7	12.0	78.9	0
South Haven	81	18.1	13.9	14.9	3.21 to 110	14.8	81.9	0
Bondville	81	22.1	16.1	16.3	5.32 to 137	18.3	82.5	0

3.1.3.1 Geographical Variation

Mean precipitation-phase mercury concentrations ranged from 15.2 ng/L at Sleeping Bear Dunes to 26.1 ng/L at IIT Chicago (Table 3-4). In addition to the mean concentrations listed, means were also calculated on a volume-weighted basis, which ranged from 11.0 ng/L at Sleeping Bear Dunes to 21.1 ng/L at IIT Chicago. Volume-weighting was done to minimize biases occurring due to small precipitation events (low bias). The variability of the sample volumes collected at each station was high, with relative standard deviations (RSDs) of approximately 100%. However, the volumes themselves did not differ

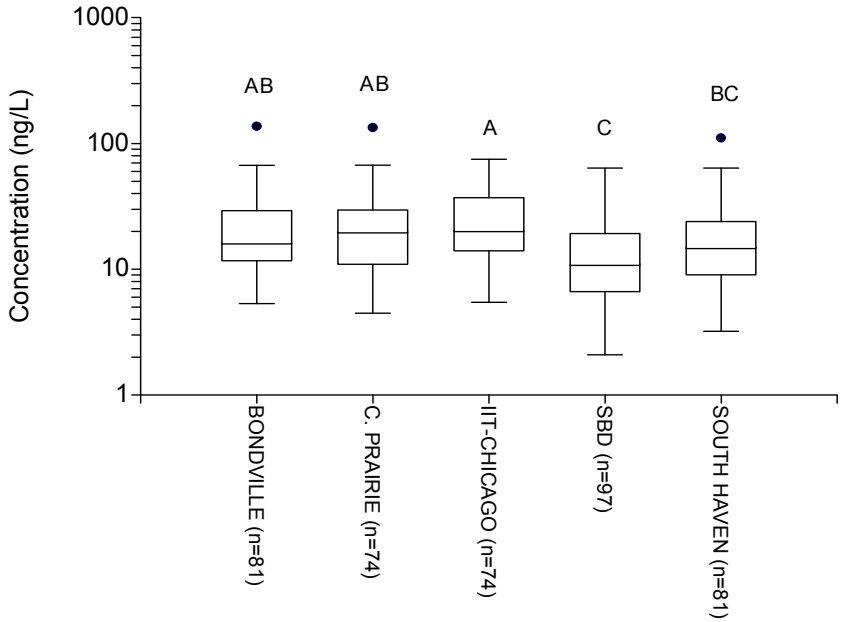
greatly between stations, and the differences in volume-weighted means between stations were consistent with the differences in arithmetic means. The formula for volume-weighted means is presented below:

$$\frac{\sum_{i=1}^{n} c_i \times v_i}{\sum_{i=1}^{n} v_i}$$

where: c_i = measured concentration in the *i*th sample,
v_i = volume of the *i*th sample, and
n = number of samples.

Arithmetic means were compared using a one-way ANOVA model with the Tukey method for pairwise comparisons. 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 also significantly lower than that at IIT Chicago. The difference between IIT Chicago and the other stations for the precipitation phase is smaller than for the vapor and particulate phases. This is likely due to the lack of an extremely high concentrations collected from this station. During a rain event, mercury is very rapidly flushed out the atmosphere; hence, the first rain during an event has the highest mercury concentrations. Therefore, short duration rain events have higher mercury concentrations than long duration events because the lower mercury concentrations of rain later in an event tend to dilute the high concentrations received early in an event. The differences in mercury concentrations at the five stations are shown in Figure 3-5.

Figure 3-5. Mercury Concentrations in Atmospheric Precipitation Measured at Four Lake Michigan Shoreline Sites and One Out-of-basin Site (Bondville)



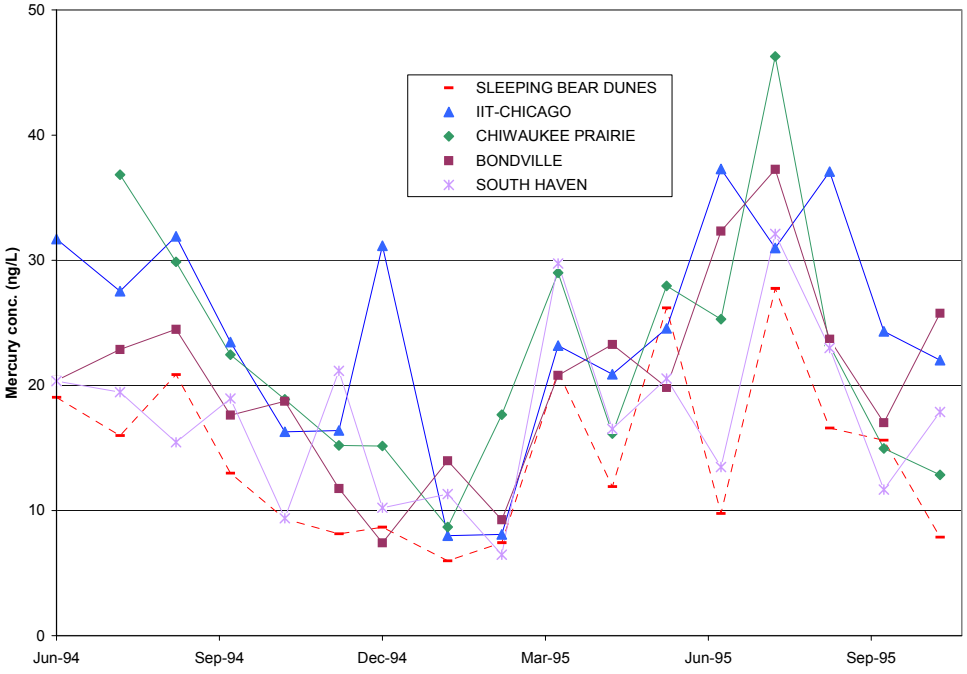
Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). C. Prairie = Chiwaukee Prairie, SBD = Sleeping Bear Dunes.

3.1.3.2 Seasonal Variation

Beginning in June 1994, samples were collected at least once during each month at each station except for Chiwaukee Prairie, based on the occurrence of precipitation events. Sampling at Chiwaukee Prairie began in July 1994. Monthly mean concentrations were calculated directly and through volume-weighting at each station, and are presented as time plots in Figures 3-6 and 3-7, respectively.

Generally, a seasonal pattern can be seen when looking at the arithmetic means, with concentrations greatest during the summer, and lowest during the winter. The only exception to this occurred in December 1994 at IIT Chicago, which had a relatively high mean concentration of 31.2 ng/L. The maximum monthly mean occurred in July 1995 for all stations except IIT Chicago, for which it occurred in June 1995. Based on one-way ANOVA models using the Tukey method for pairwise comparisons, there were significant differences in mean concentration between seasons at four of the five stations (Bondville: p=0.0166, Chiwaukee Prairie: p=0.0045, IIT Chicago: p=0.0170, Sleeping Bear Dunes: p=0.0008). At Chiwaukee Prairie, the mean concentration in summer was significantly greater than the mean concentration in autumn, while the mean concentration in summer was greater than the mean in winter at IIT Chicago. At Sleeping Bear Dunes, the mean concentration in summer was significantly greater than those in both autumn and winter, and the mean concentration in spring was also greater than the mean in autumn. No significant pairwise differences were found at Bondville. Unlike the vapor and particulate phases, there were no significant differences between years for any of the stations.

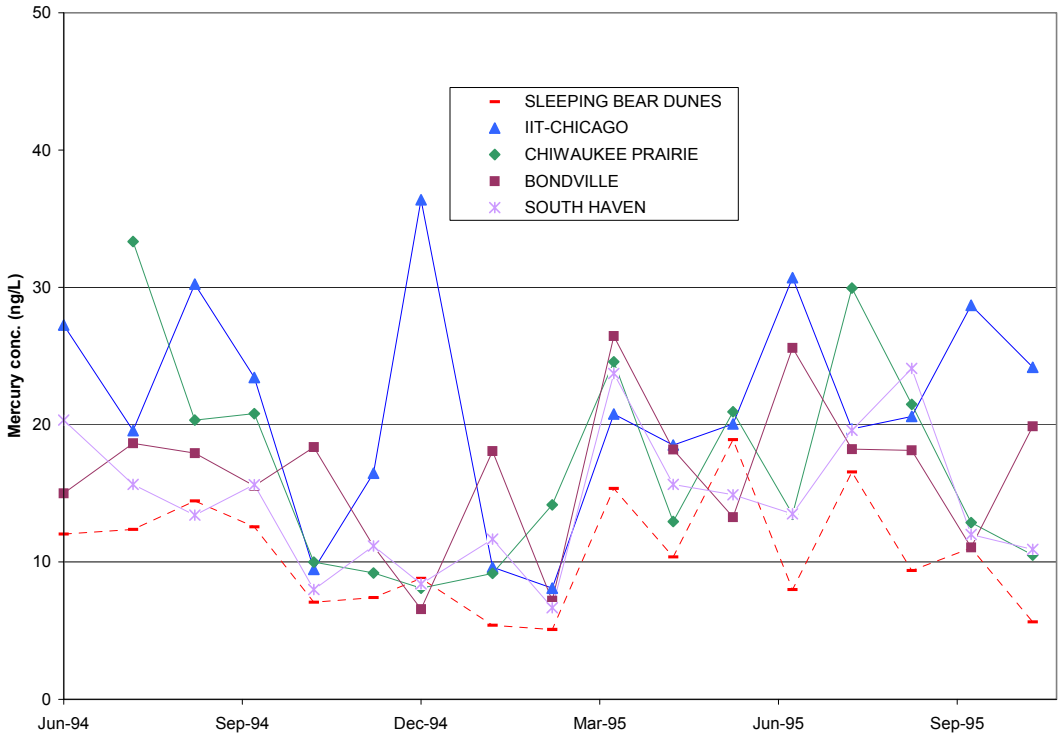
Figure 3-6. Arithmetic Monthly Means at each Station - Precipitation Phase



The seasonal pattern is less distinct when examining the volume-weighted means. Maximum monthly volume-weighted means occurred in different seasons for each station: in July 1994 at Chiwaukee Prairie, in March 1995 at Bondville, in May 1995 at Sleeping Bear Dunes, in August 1995 at South Haven, and in December 1994 at IIT Chicago. This last mean was the maximum at all stations, and contradicts the expectations based on the seasonal patterns exhibited in Figure 3-6. This value was based on three

samples, including one collected on December 4, 1994, with a volume of 170 mL and a concentration of 60.2 ng/L. All other precipitation samples with concentrations exceeding 60 ng/L had sample volumes ranging from 22 to 83 mL. Therefore, this sample had a greater effect on the monthly volume-weighted mean concentration than other high concentration, lower-volume samples. For example, a sample collected at South Haven one week before had a concentration of 63.6 ng/L, but a volume of only 34 mL.

Figure 3-7. Volume-Weighted Monthly Means at each Station - Precipitation Phase



3.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of standard operating procedures (SOPs), training of laboratory and field personnel, and establishment of method quality objectives (MQOs) for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of atmospheric mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and quality control (QC) sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 3-5 provides a summary of flags applied to the atmospheric mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. One result for vapor mercury was qualified as invalid, and was not used in the analyses of atmospheric mercury concentrations presented in this report.

Table 3-5. Summary of Routine Field Sample Flags Applied to Mercury in Atmospheric Samples

Flag	Number of QC Samples			Percentage of Samples Flagged (%)		
	Particulate	Precipitation	Vapor	Particulate	Precipitation	Vapor
LOB, Low Biased Result	—	—	—	1% (5)	0	0
INV, Invalid Result	—	—	—	0	0	0.3% (1)
FFD, Failed Field Duplicate	—	33	—	—	1% (2)	—
FFT, Failed Trip Blank	43	—	45	1% (2)	0	0.3% (1)
FPC, Failed Lab Performance Check	219	846	375	1% (5)	0	0
MDL, Below Method Detection Limit	NA	—	NA	NA	0	NA
SDL, Below System Detection Limit	—	NA	—	0	NA	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.
NA = Not Applicable

The analytical sensitivity of precipitation routine field samples was assessed through comparison to a method detection limit (MDL) of 0.300 ng/L. For particulate and vapor field samples, analytical sensitivity was assessed through comparison to system detection limits (SDL) equaling 1.00 pg/m^3 and 0.200 ng/m^3, respectively. If a sample result was below its appropriate limit, a "below MDL" or "below SDL" flag was to be applied to that sample. However, because all sample concentrations were above the corresponding limit, the MDL and SDL flags were not applied to any sample.

Field trip blanks were analyzed to assess the potential for contamination of routine field samples. A total of 88 trip blanks were analyzed, 45 in the vapor phase, and 43 in the particulate phase. In accordance with the researcher's data qualifying rules, samples were flagged for trip blank contamination (FTB) if the associated blank concentration exceeded the SDL expressed as a mass (43.45 pg for particulate samples and 0.084 ng for vapor samples). In the particulate phase, two samples were flagged for trip blank contamination, based on associated blank masses 68.2 pg and 79.1 pg. The flagged particulate routine field sample results, when expressed as masses, were approximately two and ten times the associated blank masses. One additional sample in the vapor phase was flagged for blank contamination due to an associated blank mass of 0.205 ng. The flagged vapor sample had a mass approximately 5 times greater than the associated blank mass.

A total of 33 field duplicate samples were collected and analyzed to assess precision for the precipitation phase. Field duplicates were collected at three of the five stations from which precipitation samples were collected. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD) if the relative percent difference (RPD) between results for a sample and its duplicate was greater than 25%. Two field duplicate pairs failed to meet this criteria,

with RPDs of 25.7% and 62.5%. No field duplicate samples were collected for the particulate or vapor phases; therefore, the FFD flag was not applied to any samples from these phases.

Laboratory performance check samples were used to monitor analytical bias. Performance check samples were run after every 6 samples, resulting in 1,440 total check samples. In accordance with the researcher's data qualifying rules for performance checks, field samples were flagged for a failed performance check (FPC) if the absolute percent difference for the associated performance check was greater than 20%. The FPC flag was applied to five particulate field samples, due to performance check percent differences of -28.8% and -29.1% (corresponding to percent recoveries of 71.2% and 70.9%, respectively). These five samples were also qualified as being low biased by the QC Coordinator due to the performance check recoveries. No other samples were qualified as being low biased or high biased based on analyses of performance checks, blank contamination, or other internal QC data.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 3-6 provides a summary of data quality assessments for several of these attributes for atmospheric data.

Table 3-6. Data Quality Assessment for Mercury in Atmospheric Samples

Parameter	Assessment		
	Particulate	Precipitation	Vapor
Number of Routine Samples Analyzed	399	407	393
System Precision, Mean Field Duplicate RPD (%), >SDL	—	9.78% (33)	—
Analytical Bias, Mean LPC RPD%	- 2.20% (219)	0.823% (846)	- 1.51% (375)
Analytical Sensitivity, Samples reported as <SDL or MDL (%)	0	0	0

Number of QC samples used in the assessment is provided in parentheses
SDL = System detection limit
LPC = Laboratory performance check

The mean RPD between routine field samples and field duplicates for mercury in precipitation was 9.78%, indicating good precision. Because field duplicates were collected and reported for the precipitation phase only, no estimate of system precipitation could be made for the particulate and vapor phases. For these two phases, the PI collected and analyzed collocated samples. Because collocated samples were collected at only one of the sites and because the sampling times for these samples were shorter than for the routine field samples, these results may not fully represent the variability that may have been observed for field samples. Therefore, results for the collocated samples were not used in the QA assessment.

Analytical results for laboratory duplicates were not reported as individual results. The PI reported average results; however, the number of replicates that were included in the average or the standard deviation of those results were not provided. Based on submitted results, the results for laboratory duplicates could not be verified. Therefore, no estimate of analytical precision could be made for the atmospheric data.

Analytical bias was evaluated by calculating the mean RPD of laboratory performance check samples (LPC). Results indicated very little overall bias for analytical results. Mean LPC RPDs for the three

phases ranged from -2.20% for particulate to 0.823% for precipitation. When expressed as percent recoveries, these means correspond to 97.8% and 101%, respectively.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the SDL for precipitation data and the percentage of samples reported below the MDL for the particulate and vapor data. This percentage was 0% for all three phases.

3.3 Data Interpretation

3.3.1 Atmospheric Sources

Based on the results of this study, vapor, particulate and precipitation phases were all important sources of mercury to Lake Michigan. All results from all three phases were above the associated method or system detection limit. The mean vapor and particulate mercury concentrations of 2.44 ng/m^3 and 30.7 pg/m^3 (0.0307 ng/m^3) were approximately 12 and 30 times greater than their associated SDLs. The mean precipitation-phase mercury concentration of 20.6 ng/L was approximately 70 times greater than the associated MDL.

3.3.2 Seasonal Considerations

Generally, the effect of season on mercury concentration depended on the phase and the station from which the samples were collected. For vapor-phase mercury, significant differences between seasons were observed only at IIT Chicago and Chiwaukee Prairie, with peak concentrations during the summer at both stations. Both of these stations had greater levels in the summer of 1994 compared to 1995. For particulate-phase mercury, significant seasonal differences were observed only at Sleeping Bear Dunes, with peak concentrations occurring during the summer.

Seasonal patterns were most apparent in precipitation-phase mercury. Significant differences between seasons occurred at four of the five stations. For each of these stations, the peak concentrations occurred in summer and the lowest concentrations occurred either during autumn or winter. However, these seasonal differences may have been partly due to the occurrence of smaller precipitation events during the summer, compared to other seasons, which would result in smaller sample volumes, and hence, higher mercury concentrations, during the initial wash out of mercury from the atmosphere.

When the data were examined using volume-weighted means, seasonal patterns became much less distinct. However, for all stations other than Chicago IIT, the lowest volume-weighted means did occur during the winter. This may have been due to differences in precipitation type, as the relationship between mercury and precipitation may differ between warm-cloud processes and cold-cloud processes (Landis *et al.*, 2002). In a study of precipitation in mercury in the Lake Superior region, Glass *et al.* (1986) found significantly greater mercury concentrations in rainfall than in snow. The seasonal pattern was also similar to that observed at three sites in Wisconsin as part of the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (WDNR, 1999). Volume-weighted mean concentrations in that study were highest in the spring or summer for each site for all three years, other than for one site in 1995, where the mean concentration was highest in the winter.

Significant differences between seasons were observed at only one LMMB station for particulate-phase mercury. At the Sleeping Bear Dunes site, the mean concentration during summer was significantly greater than the mean concentration during winter. This result is not consistent with results from past studies. Particulate-phase mercury concentrations have previously been observed to be greater during the winter compared to the summer in Maryland (Mason *et al.*, 1997) and near Lake Michigan (Keeler *et al.*,

1995). Concentrations at Sleeping Bear Dunes were similar during the two summers for which data were collected.

3.3.3 Regional Considerations

For particulate and vapor-phase mercury, the mean concentration at IIT Chicago was significantly greater than those at the other stations. For precipitation-phase mercury, the mean concentration was also greatest at IIT Chicago, and was significantly higher than at two of the other stations. This was not unexpected, as IIT Chicago was the only one of the five stations that could be classified as being located in an urban area. It has been observed in the past that the Chicago area has significantly increased mercury levels in dry deposition (Keeler, 1994) and precipitation around local urban/industrial areas (Hoyer *et al.*, 1995). The difference between IIT Chicago and the other stations was greater for particulate-phase mercury than for the other phases. This may be due to the greater prevalence of the mercuric form of mercury (Hg^{2+}) in the particulate phase compared to the vapor phase. Mercuric mercury is more soluble in water, and therefore more likely to be due to local sources (Lindberg and Stratton, 1998). Mason *et al.* (1997) found low levels of ionic mercury in precipitation, and hypothesized that this was due to in-cloud oxidation processes being a significant source of mercury in precipitation, rather than just the scavenging of particles or of gaseous ionic mercury.

The mean and median vapor-phase concentrations at IIT Chicago (mean: 3.62 ng/m^3, median: 2.90 ng/m^3) were very close to those collected in Egbert, Ontario in 1990 (mean: 3.71 ng/m^3, median: 2.90 ng/m^3) by Schroeder and Markes (1994). The station at IIT Chicago represents a major urban/industrial area and the station in the Ontario study was located near Toronto, another major urban/industrial area. Thus, the results from both studies may represent the influences of urban and industrial sources of mercury. However, the samples from the Ontario study were all collected in the months of March and April, and therefore cannot be interpreted as an annual estimate. The 49 mercury samples collected at IIT Chicago in March and April 1995 had a mean of 2.26 ng/m^3 and a median of 2.14 ng/m^3, substantially lower than the overall values. In addition to collecting samples in Egbert, Ontario, Schroeder and Markes (1994) also measured mercury at Pt. Petre, Ontario. This site had lower mercury concentrations, with a mean of 2.21 ng/m^3, comparable to the other stations in the LMMB data set. The Pt. Petre samples were collected in the autumn only, however, and the LMMB stations had slightly lower results during these months.

While the difference in mean precipitation-phase mercury concentrations at IIT Chicago and the other stations was not as large compared to the other phases in the study, the mean concentration at IIT Chicago was still higher than for many sites in other studies. For example, samples of mercury in precipitation have recently been collected as part of the National Atmospheric Deposition Program's Mercury Deposition Network (MDN). The volume-weighted mean calculated from the MDN transition phase in 1995 was 10.25 ng/L, lower than the mean at all five LMMB stations (MDN, 1999). In addition, in an assessment using data collected as part of the NADP, volume-weighted mean concentrations were calculated for samples collected from seven sites in Wisconsin from 1995 to 1997 (WDNR, 1999). The state-wide volume-weighted means for the three years ranged from 11.48 ng/L in 1997 to 15.75 ng/L in 1995. These means are similar to the volume-weighted mean concentrations from Chiwaukee Prairie (16.5 ng/L), Bondville (16.1 ng/L), and South Haven (13.9 ng/L), but below the volume-weighted mean of 21.1 ng/L from IIT Chicago. However, the maximum annual volume-weighted mean of 25.60 ng/L from the seven Wisconsin sites, occurring at the rural Wildcat Mountain State site in western Wisconsin in 1996, exceeded the volume-weighted mean at IIT Chicago. This mean was based on the results from one of two sampling columns at that site, with the other column yielding in a mean of 13.81 ng/L. It is worth noting that the mean concentration from this second column was greater than that of Sleeping Bear Dunes (11.0 ng/L), the only atmospheric site from the LMMB located in a similarly rural area.

Other recent studies have also shown spatial differences in mercury concentration in precipitation. Mason *et al.* (2000) found higher levels of mercury flux at a site in Baltimore, compared to three other rural sites in Maryland. Glass *et al.* (1986) measured mercury concentrations in snow pack collected from three areas in Minnesota, one in Wisconsin, one in Upper Peninsula of Michigan, and one in Ontario within watersheds that drain into Lake Superior. Samples of snow pack were collected at 10 to 17 specific locations in each of these geographic areas. Measurements of mercury in snow from five of the six areas were below those of IIT Chicago in this study. The means from these five areas ranged from 12 ng/L to 15 ng/L, with standard deviations ranging from 1 to 5 ng/L. The sixth sampling area was centered around Grand Rapids, Minnesota, and had a mean concentration of 100 ng/L and a standard deviation of 173 ng/L. The mean concentration is substantially higher than the mean at IIT Chicago in this study, and may be the result of contamination of samples from that area, or may represent a localized source of mercury. In addition, the results may not be comparable to all of the LMMB data, because the samples were collected in snow, rather than rain.

Chapter 4
Mercury in Tributaries

4.1 Results

From March 29, 1994 to October 31, 1995, samples were collected from 11 tributaries that flow into Lake Michigan (Figure 2-3 in Chapter 2). Samples were collected as described in Section 2.4.2 and analyzed for total and dissolved mercury by cold-vapor atomic fluorescence spectrometry (see Section 2.5.2). A total of 346 samples were collected and analyzed for dissolved mercury, and 353 samples were collected and analyzed for total mercury (Table 4-1). In addition to the analysis of total and dissolved mercury, a subset of samples was analyzed for methylmercury using a combination of distillation, ethylation, gas chromatography, and cold-vapor atomic fluorescence spectrometry. A total of 203 samples were analyzed for total methylmercury, and 204 samples were analyzed for dissolved methylmercury.

Table 4-1. Number of Tributary Samples Analyzed for Mercury and Methylmercury

Analyte	Tributary	Sampling Dates	Number of Samples Analyzed		Total Number of Samples Analyzed
			Dissolved Fraction	Total Fraction	
Mercury	Fox	04/07/94 to 10/12/95	38	39	77
	Grand Calumet	08/04/94 to 10/18/95	15	15	30
	Grand	04/11/94 to 10/31/95	46	47	93
	Kalamazoo	04/12/94 to 10/30/95	38	38	76
	Manistique	04/11/94 to 10/26/95	27	27	54
	Menominee	04/13/94 to 10/11/95	23	25	48
	Milwaukee	03/29/94 to 10/06/95	36	38	74
	Muskegon	04/14/94 to 10/17/95	27	27	54
	Pere Marquette	04/05/94 to 10/18/95	28	28	56
	Sheboygan	04/06/94 to 09/19/95	35	36	71
	St. Joseph	04/06/94 to 10/27/95	33	33	66
		Total	346	353	699
Methylmercury	Fox	01/11/95 to 08/30/95	17	15	32
	Grand Calumet	02/13/95 to 10/18/95	7	8	15
	Grand	04/28/94 to 10/31/95	31	33	64
	Kalamazoo	01/26/95 to 10/30/95	16	14	30
	Manistique	04/11/94 to 10/26/95	20	21	41
	Menominee	01/17/95 to 10/11/95	12	12	24
	Milwaukee	01/10/95 to 10/06/95	21	21	42
	Muskegon	01/24/95 to 10/17/95	11	11	22
	Pere Marquette	04/05/94 to 10/18/95	22	20	42
	Sheboygan	04/14/94 to 10/24/95	32	32	64
	St. Joseph	01/27/95 to 10/27/95	15	16	31
		Total	204	203	407

4.1.1 Geographical Variation

4.1.1.1 Mercury

Total mercury concentrations measured in Lake Michigan tributaries ranged from 0.536 to 191 ng/L. In the 11 tributaries monitored in the LMMB Study, mean total mercury concentrations ranged from 1.07 ng/L in the Muskegon River to 28.9 ng/L in the Fox River (Table 4-2). Analysis of variance (and Tukey's pairwise comparison test) revealed that total mercury concentrations in the Fox River were significantly higher than in any other Lake Michigan tributary (Figure 4-1). The mean total mercury concentration in the Fox River was 2.7 to 27 times higher than in other Lake Michigan tributaries. The Fox River watershed has long been highly industrialized and Hurley *et al.* (1998a) have suggested that the main source of Fox River mercury loads is resuspension of contaminated sediments. Following the Fox River, total mercury concentrations were highest in the Kalamazoo and Grand Calumet Rivers. Total mercury concentrations in these tributaries were significantly higher (at the 95% confidence level) than in any other tributary, except for the Fox River. These rivers are located to the south and southeast of Lake Michigan (Figure 4-2), where urban and industrial land uses are predominant. The lowest total mercury concentrations were observed in the Muskegon, Pere Marquette, Manistique, and Menominee Rivers (Figure 4-2), which are the more northern tributaries that are primarily forested. Total mercury concentrations in the Muskegon River were significantly lower than any other Lake Michigan tributary (Figure 4-1). Hurley *et al.* (1998b) explained that the low mercury concentrations in this tributary may be due to Lake Muskegon, which is located directly upstream of the sampling site and acts as a temporary sink for contaminants.

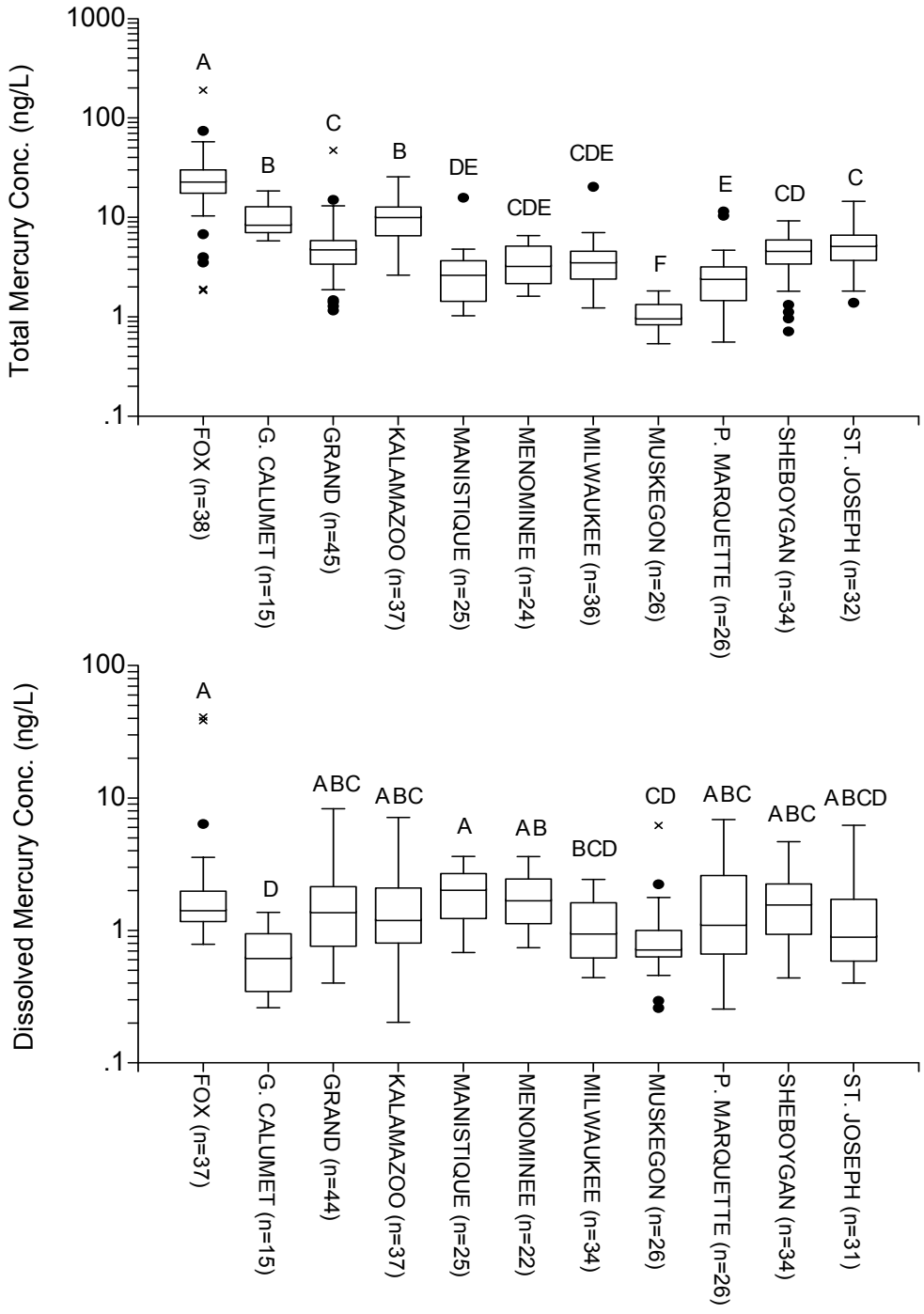
Dissolved mercury concentrations were more consistent among tributaries than total mercury concentrations. Mean dissolved mercury concentrations only ranged from 0.666 ng/L in the Grand Calumet River to 3.71 in the Fox River. The remaining tributaries all contained mean dissolved mercury levels between 1 and 2 ng/L (Table 4-2). Fewer significant differences in dissolved mercury concentrations also were seen among tributaries (Figure 4-1 and Figure 4-2). Unlike total mercury concentrations, dissolved mercury concentrations in the Fox River were not significantly higher than in all other tributaries. Dissolved mercury concentrations in the Fox River were only significantly higher than in three other tributaries (Grand Calumet, Muskegon, and Milwaukee Rivers). Following the Fox River, mean dissolved mercury concentrations were highest in the Manistique and Menominee Rivers, two tributaries that had among the lowest concentrations of total mercury. Dissolved mercury concentrations in the Manistique River were significantly higher than in three other tributaries, and dissolved mercury concentrations in the Menominee River was significantly higher than in two other tributaries. The lowest mean dissolved mercury concentration was in the Grand Calumet River, which was among the highest in total mercury concentrations. The mean dissolved mercury concentration at this site was significantly lower than in seven other tributaries.

Table 4-2. Mean Mercury Concentrations Measured in Lake Michigan Tributaries

Fraction	Tributary	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Dissolved	Fox	37	3.71	1.44	0.786 to 40.8	8.75	236	0.00
	Grand Calumet	15	0.666	0.628	0.261 to 1.37	0.341	51.2	0.00
	Grand	44	1.68	1.39	0.400 to 8.29	1.32	78.9	0.00
	Kalamazoo	37	1.62	1.22	0.202 to 7.12	1.41	87.3	0.00
	Manistique	25	1.99	2.06	0.680 to 3.61	0.815	40.9	0.00
	Menominee	22	1.87	1.71	0.739 to 3.61	0.861	46.1	0.00
	Milwaukee	34	1.15	0.963	0.439 to 2.42	0.594	51.7	0.00
	Muskegon	26	1.08	0.730	0.259 to 6.20	1.13	105	0.00
	Pere Marquette	26	1.79	1.12	0.254 to 6.86	1.56	87.0	0.00
	Sheboygan	34	1.64	1.59	0.437 to 4.68	0.928	56.5	0.00
	St. Joseph	31	1.46	0.912	0.399 to 6.21	1.42	97.2	0.00
Particulate[a]	Fox	37	25.8	22.1	-11.3 to 153	26.2	101	—
	Grand Calumet	15	9.26	8.00	4.68 to 18.2	4.34	46.9	—
	Grand	43	4.29	3.23	-3.54 to 46.6	7.16	167	—
	Kalamazoo	37	9.00	8.81	0.786 to 23.7	5.56	61.8	—
	Manistique	25	1.08	0.447	-0.0865 to 13.3	2.61	242	—
	Menominee	22	1.92	1.75	-0.339 to 4.81	1.57	81.7	—
	Milwaukee	34	2.93	2.45	-0.320 to 18.6	3.06	104	—
	Muskegon	26	-0.0058	0.215	-4.96 to 0.742	1.08	—	—
	Pere Marquette	26	1.09	0.758	-5.40 to 7.67	2.49	228	—
	Sheboygan	33	3.02	3.12	-0.0094 to 7.42	1.59	52.9	—
	St. Joseph	31	4.04	4.18	-1.73 to 9.24	2.33	57.6	—
Total	Fox	38	28.9	23.5	1.84 to 191	30.5	106	0.00
	Grand Calumet	15	9.93	8.63	5.81 to 18.5	4.29	43.2	0.00
	Grand	45	6.02	4.87	1.16 to 47.5	6.91	115	0.00
	Kalamazoo	37	10.6	10.3	2.62 to 25.7	5.77	54.3	0.00
	Manistique	25	3.07	2.71	1.02 to 15.8	2.89	94.2	0.00
	Menominee	24	3.63	3.33	1.61 to 6.57	1.57	43.3	0.00
	Milwaukee	36	4.08	3.62	1.23 to 20.3	3.19	78.1	0.00
	Muskegon	26	1.07	0.984	0.536 to 1.82	0.354	33.1	0.00
	Pere Marquette	26	2.88	2.46	0.557 to 11.5	2.59	90.1	0.00
	Sheboygan	34	4.52	4.72	0.712 to 9.25	2.00	44.1	0.00
	St. Joseph	32	5.40	5.29	1.38 to 14.5	2.70	50.1	0.00

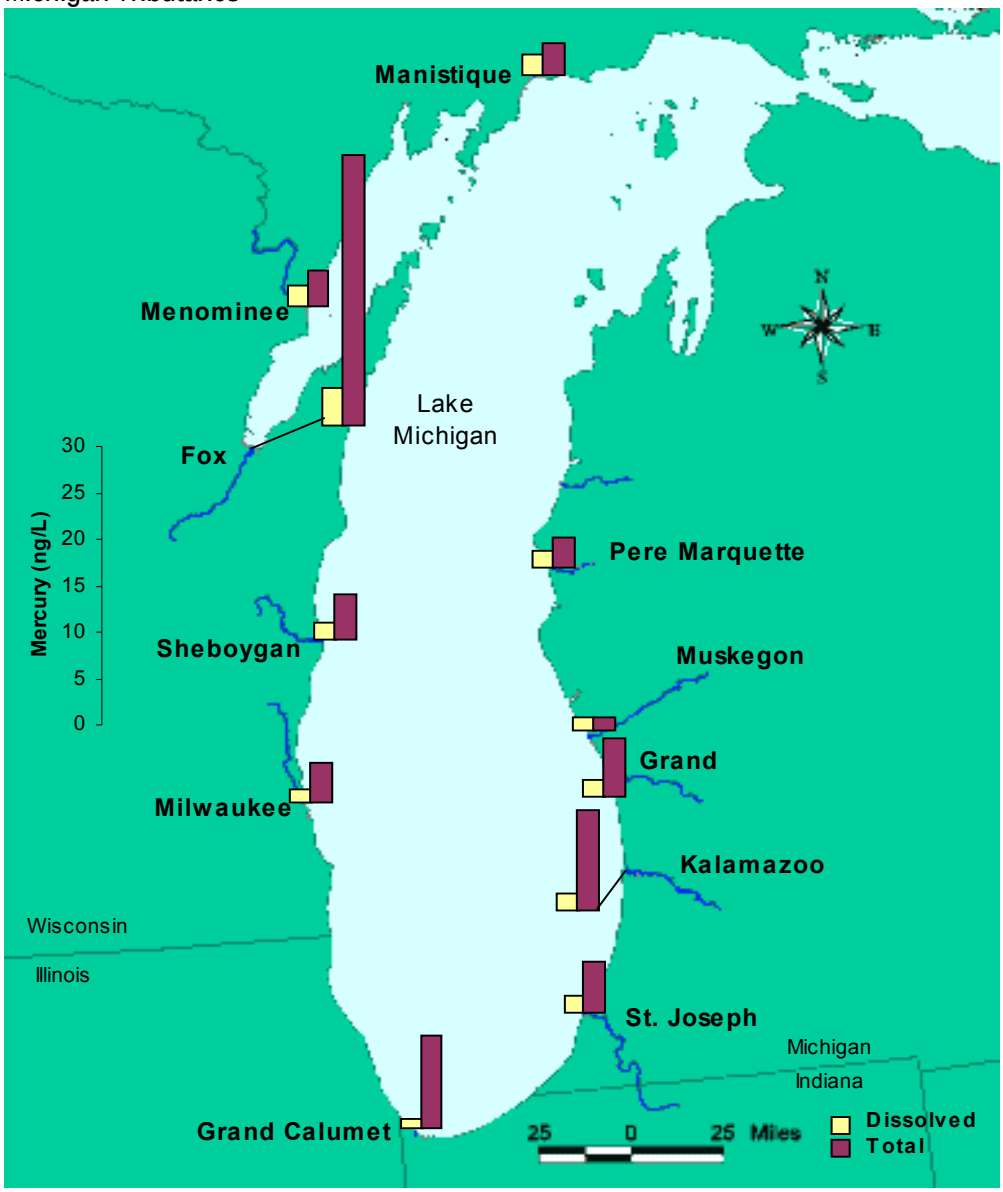
[a] Mercury concentrations in the particulate fraction were not directly measured. Particulate concentrations for each sample were calculated as the difference between the measured total and dissolved concentrations. If measured dissolved concentrations were greater than measured total concentrations, the calculated concentration in the particulate fraction was a negative number. Because particulate concentrations were calculated from two measured values, these reported concentrations will contain more variability than measured values reported for dissolved and total fractions. Also, the percent of samples below the detection limit could not be determined for the particulate fraction, because this fraction was not directly measured and detection limits for this fraction were not developed.

Figure 4-1. Total and Dissolved Mercury Concentrations in Lake Michigan Tributaries



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Figure 4-2. Mean Total and Dissolved Mercury Concentrations Measured in Lake Michigan Tributaries



4.1.1.2 Methylmercury

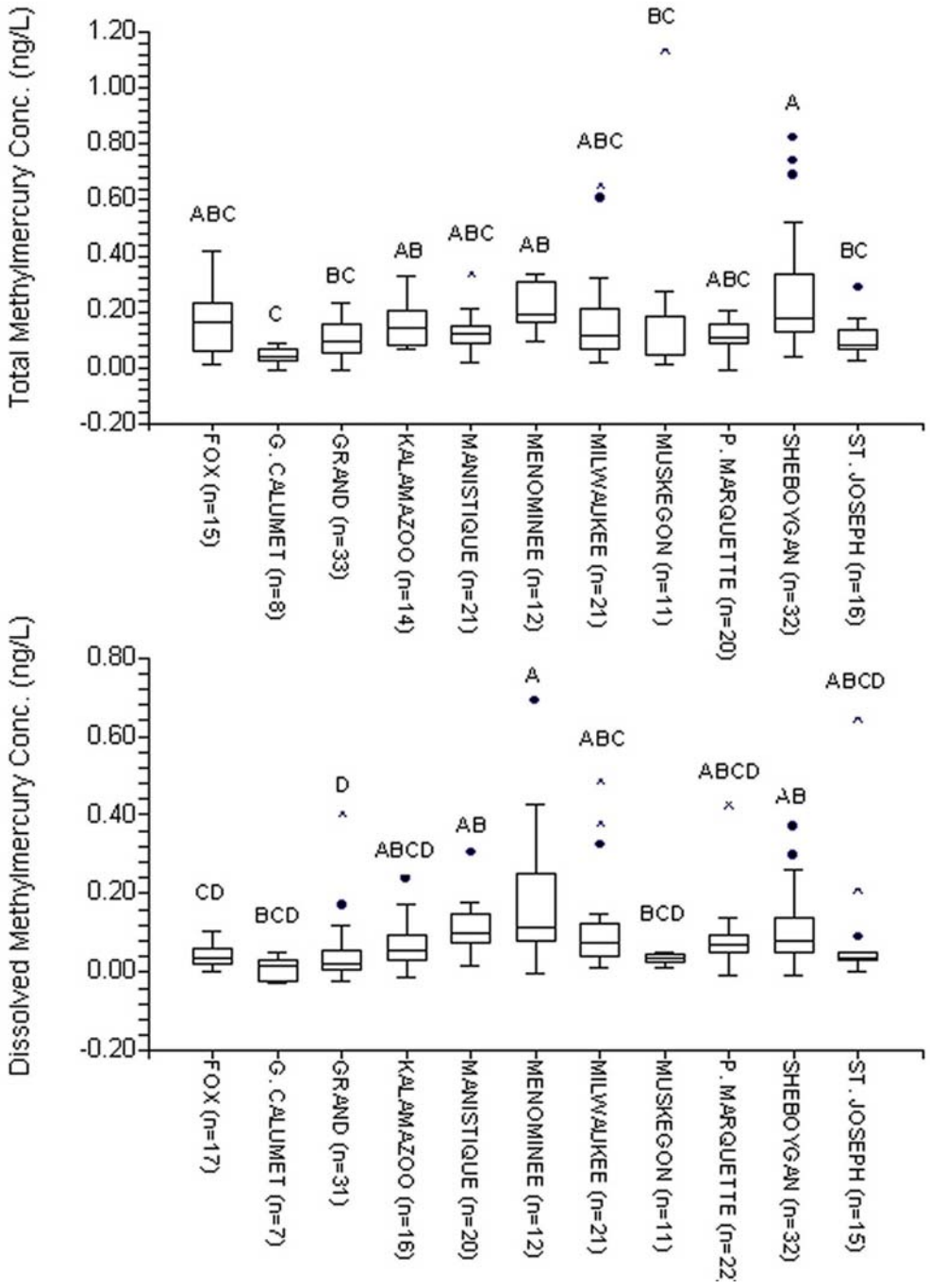
The geographical pattern of methylmercury concentrations in Lake Michigan tributaries was very different from that of total mercury. While total mercury concentrations were much higher in the Fox River than in other tributaries, methylmercury concentrations in four other tributaries were higher than in the Fox River (Table 4-3). Mean total methylmercury concentrations in Lake Michigan tributaries ranged from 0.0424 ng/L in the Grand Calumet to 0.260 ng/L in the Sheboygan River (Table 4-3). Total methylmercury concentrations in the Sheboygan River were significantly higher than in the St. Joseph, Muskegon, Grand, and Grand Calumet Rivers (Figure 4-3). Total methylmercury concentrations in the Grand Calumet were significantly lower than in the Sheboygan, Kalamazoo, and Menominee Rivers. No other significant differences in total methylmercury were observed among Lake Michigan tributaries.

Table 4-3. Mean Methylmercury Concentrations Measured in Lake Michigan Tributaries

Fraction	Tributary	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Dissolved	Fox	17	0.0419	0.0420	0.00100 to 0.103	0.0254	60.7	23.5
	Grand Calumet	7	0.0133	0.0220	-0.0281 to 0.0527	0.0300	226	42.9
	Grand	31	0.0479	0.0240	-0.0212 to 0.404	0.0779	163	41.9
	Kalamazoo	16	0.0704	0.0620	-0.0137 to 0.240	0.0649	92.3	18.8
	Manistique	20	0.114	0.106	0.0180 to 0.304	0.0624	54.6	5.00
	Menominee	12	0.182	0.117	-0.00154 to 0.692	0.198	109	8.33
	Milwaukee	21	0.115	0.0774	0.00977 to 0.487	0.126	110	4.76
	Muskegon	11	0.0363	0.0386	0.0111 to 0.0508	0.0128	35.2	9.09
	Pere Marquette	22	0.0850	0.0733	-0.00700 to 0.428	0.0839	98.6	9.09
	Sheboygan	32	0.106	0.0860	-0.00868 to 0.371	0.0848	79.7	3.13
	St. Joseph	15	0.0915	0.0393	0.000980 to 0.645	0.161	175	6.67
Particulate[a]	Fox	15	0.118	0.134	-0.0300 to 0.398	0.115	97.8	—
	Grand Calumet	7	0.0309	0.0274	-0.0162 to 0.112	0.0494	160	—
	Grand	29	0.0492	0.0500	-0.225 to 0.172	0.0762	155	—
	Kalamazoo	14	0.0809	0.0806	-0.164 to 0.344	0.115	142	—
	Manistique	19	0.0073	0.0080	-0.247 to 0.203	0.0879	1210	—
	Menominee	12	0.0351	0.0712	-0.492 to 0.268	0.214	609	—
	Milwaukee	20	0.0552	0.0370	-0.281 to 0.568	0.209	379	—
	Muskegon	11	0.148	0.0254	-0.0023 to 1.08	0.319	216	—
	Pere Marquette	20	0.0312	0.0270	-0.283 to 0.122	0.0834	268	—
	Sheboygan	29	0.139	0.0840	-0.226 to 0.767	0.193	139	—
	St. Joseph	15	0.0081	0.0474	-0.579 to 0.236	0.184	2280	—
Total	Fox	15	0.162	0.170	0.0150 to 0.413	0.106	65.3	6.67
	Grand Calumet	8	0.0424	0.0428	-0.00804 to 0.0883	0.0297	70.0	12.5
	Grand	33	0.104	0.0993	-0.00600 to 0.232	0.0593	57.0	6.06
	Kalamazoo	14	0.153	0.147	0.0647 to 0.33	0.0773	50.6	0.00
	Manistique	21	0.123	0.128	0.0210 to 0.340	0.0699	56.7	0.00
	Menominee	12	0.217	0.196	0.0971 to 0.331	0.0762	35.1	0.00
	Milwaukee	21	0.170	0.117	0.0220 to 0.651	0.170	100	0.00
	Muskegon	11	0.184	0.0537	0.00881 to 1.13	0.323	176	9.09
	Pere Marquette	20	0.116	0.110	-0.00796 to 0.202	0.0514	44.4	5.00
	Sheboygan	32	0.260	0.182	0.038 to 0.822	0.206	79.1	0.00
	St. Joseph	16	0.103	0.0846	0.0252 to 0.286	0.0639	61.8	0.00

[a] Mercury concentrations in the particulate fraction were not directly measured. Particulate concentrations for each sample were calculated as the difference between the measured total and dissolved concentrations. If measured dissolved concentrations were greater than measured total concentrations, the calculated concentration in the particulate fraction was a negative number. Because particulate concentrations were calculated from two measured values, these reported concentrations will contain more variability than measured values reported for dissolved and total fractions. Also, the percent of samples below the detection limit could not be determined for the particulate fraction, because this fraction was not directly measured and detection limits for this fraction were not developed.

Figure 4-3. Total and Dissolved Methylmercury Concentrations in Lake Michigan Tributaries



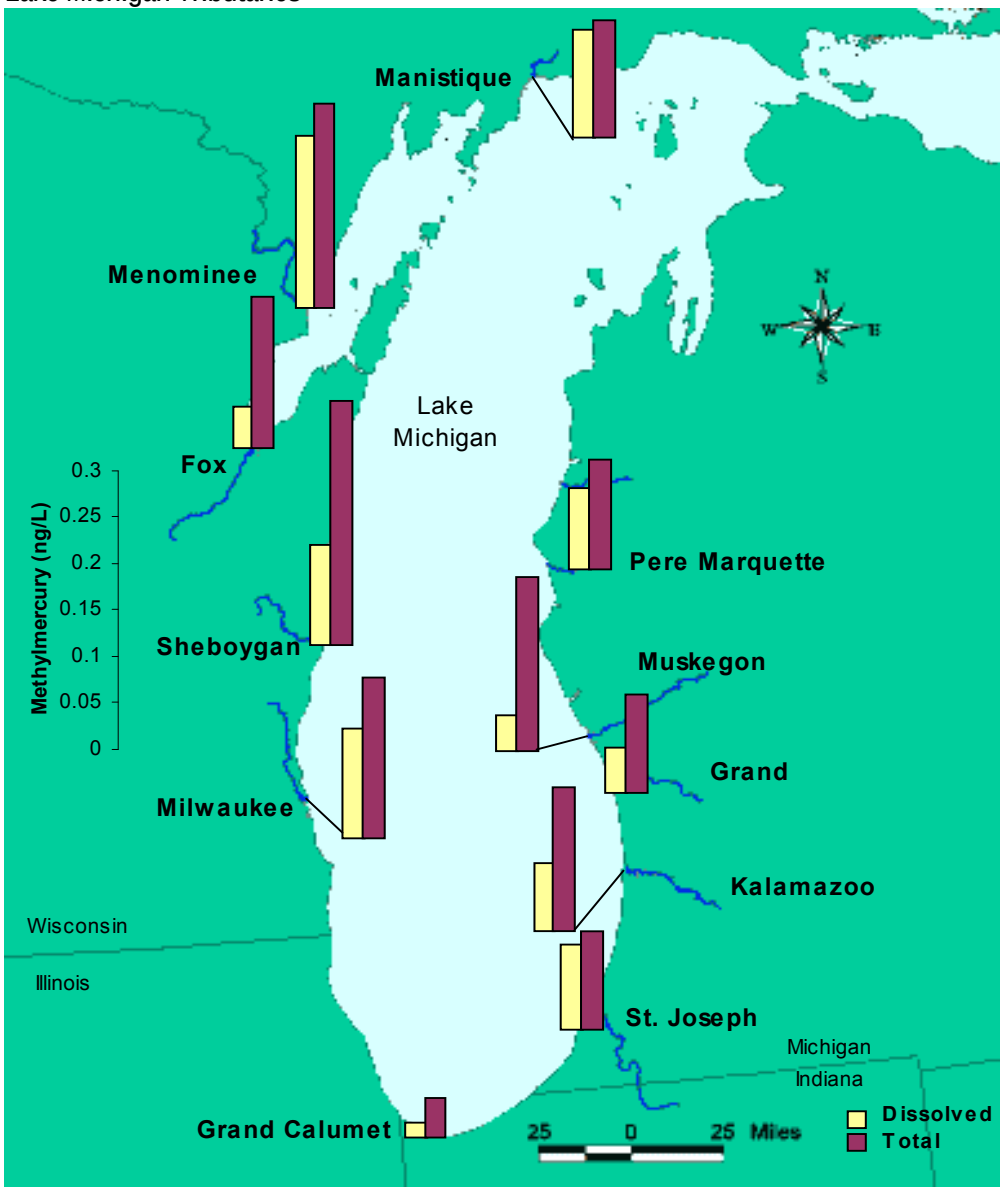
Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The geographical pattern of dissolved methylmercury concentrations in Lake Michigan tributaries also were different from that of dissolved mercury. Mean dissolved methylmercury concentrations ranged from 0.0133 ng/L in the Grand Calumet to 0.182 ng/L in the Menominee River. Dissolved

methylmercury concentrations in the Menominee were significantly higher than in the Muskegon, Fox, Grand, and Grand Calumet Rivers. Dissolved methylmercury concentrations in the Sheboygan and Manistique Rivers were significantly higher than in the Fox and Grand Rivers, and dissolved methylmercury concentrations in the Milwaukee River were significantly higher than in the Grand River.

While the more northern and forested watersheds had lower total mercury concentrations, these tributaries did not have corresponding lower concentrations of methylmercury (Figure 4-4). Methylmercury concentrations in the Manistique, Menominee, Pere Marquette, and Muskegon Rivers were not significantly lower than in any other sites, with the exception of the Muskegon River being significantly lower than the Sheboygan River in total methylmercury. Similarly, those industrialized sites that had the highest total mercury levels (Fox, Kalamazoo, and Grand Calumet Rivers), did not have corresponding high methylmercury concentrations. Total methylmercury concentrations in these tributaries were not significantly higher than in any other site.

Figure 4-4. Mean Total and Dissolved Methylmercury Concentrations Measured in Lake Michigan Tributaries



4.1.2 Seasonal Variation

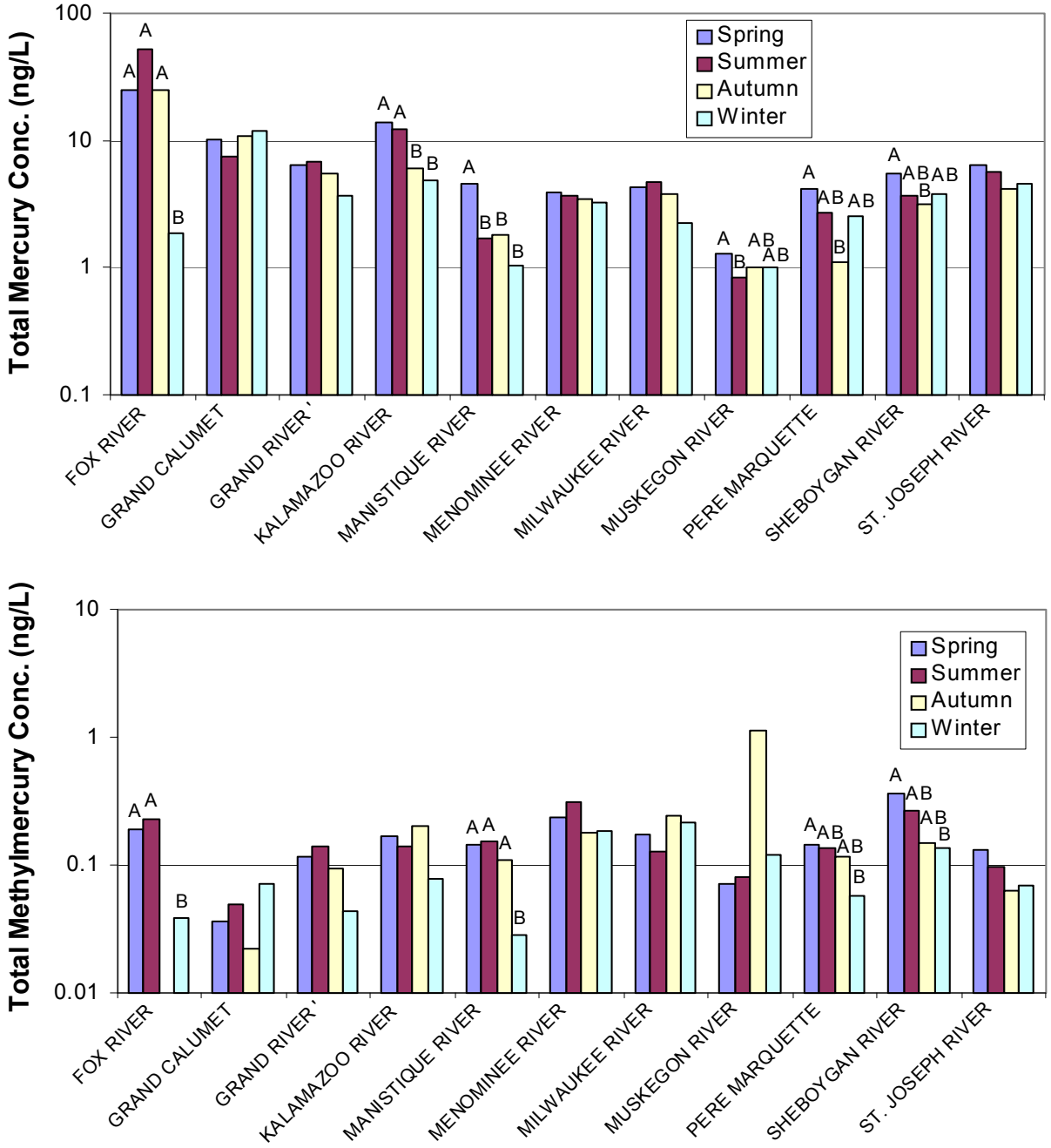
Tributary samples were collected for mercury analysis throughout seven consecutive seasons (Spring 1994 through Autumn 1995). Analysis of variance (with Tukey's pairwise comparison test) revealed that total mercury concentrations differed significantly among season in six of the eleven tributaries (Figure 4-5). In the Fox River, winter total mercury concentrations were significantly lower than in any other season. In the Kalamazoo River, winter and autumn concentrations of total mercury were significantly lower than spring or summer concentrations. In the Manistique River, spring concentrations of total mercury were significantly higher than in other seasons. In the Muskegon River, spring total mercury concentrations were significantly higher than summer concentrations. In the Pere Marquette and Sheboygan Rivers, spring total mercury concentrations were significantly higher than concentrations during autumn.

While seasonal patterns varied among tributaries, total mercury concentrations were generally higher in the spring and lower in the winter. Spring concentrations of total mercury were higher than winter values in ten of the eleven tributaries, and these differences were statistically significant in three of the tributaries. In all six tributaries that showed significant seasonal differences, total mercury concentrations were significantly higher in the spring than in other seasons.

Methylmercury concentrations differed significantly among seasons in four tributaries (Figure 4-5). In the Fox and Manistique Rivers, total methylmercury concentrations during the winter were significantly lower than in all other seasons. In the Pere Marquette and Sheboygan Rivers, total methylmercury concentrations during the winter were significantly lower than in the spring. Similar to total mercury concentrations, total methylmercury concentrations were generally higher in the spring and lower in the winter. Spring concentrations of total methylmercury were higher than winter values in eight of eleven tributaries and these differences were statistically significant in four of these tributaries.

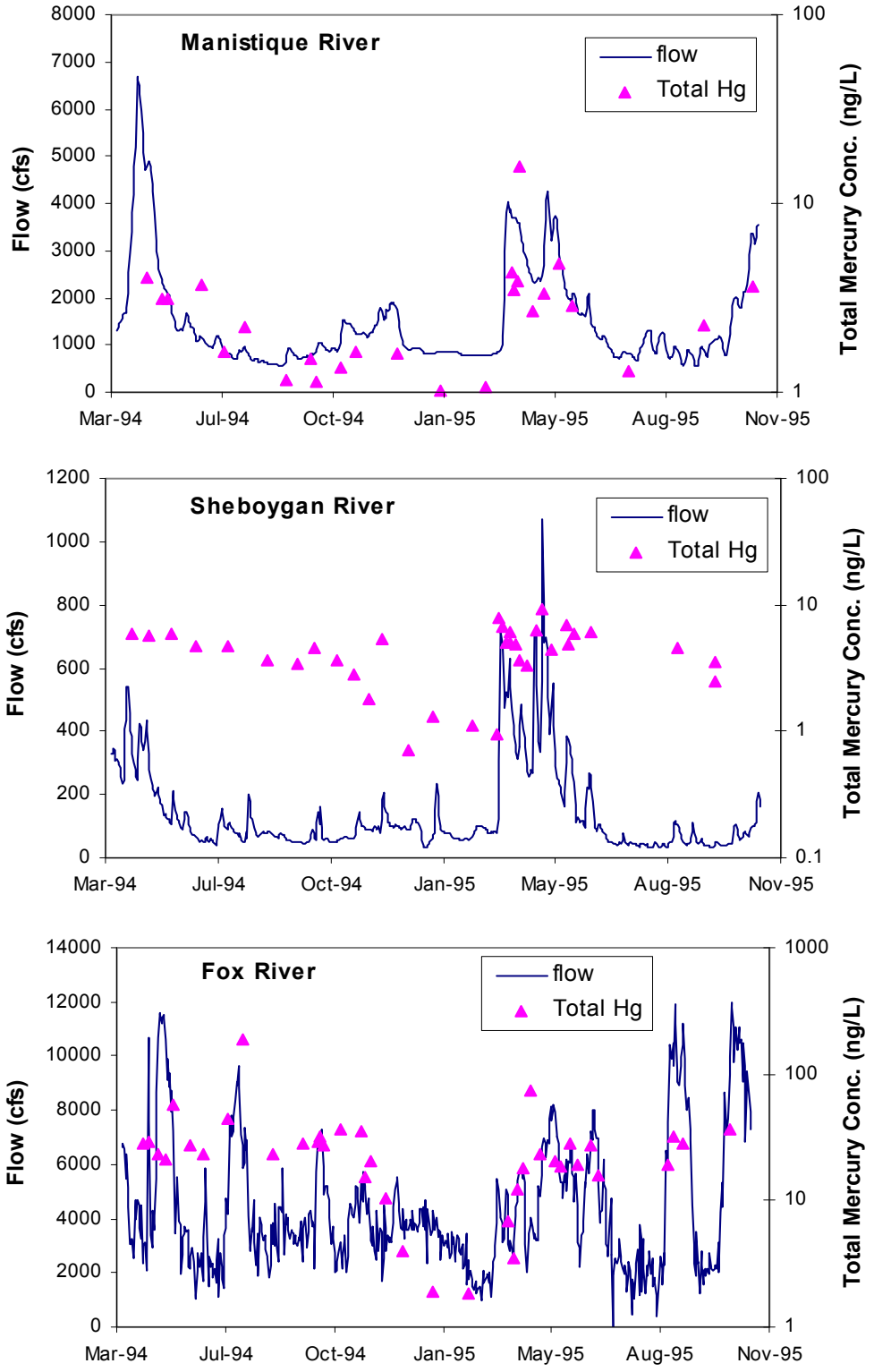
In most of the tributaries with significant seasonal differences in total mercury and methylmercury concentrations, difference were tied to the seasonal flow regimes of the tributaries. The flow regimes of many of these tributaries were dominated by high spring flows, which coincided with higher mercury concentrations. Low mercury concentrations in the winter also coincided with lower tributary flows. Figure 4-6 demonstrates this effect in the Manistique, Sheboygan, and Fox Rivers. Ice cover in the winter in many of these tributaries may also lead to reduced mixing and resuspension of contaminated sediments, which would result in lower total mercury concentrations during the winter. The hydrograph for the Fox River also demonstrates that high mercury concentrations are often associated with peak flow events throughout the year. Many of the highest total mercury concentrations measured in the Fox River coincided with high storm event flows. Indeed, tributary mercury concentrations were correlated with flow in many of the tributaries (see Section 4.1.3).

Figure 4-5. Seasonal Variation of Mercury Concentrations in Lake Michigan Tributaries



Bars with the same letter were not statistically different (at alpha = 0.05).

Figure 4-6. Seasonal Flow Patterns and Total Mercury Concentrations in Selected Lake Michigan Tributaries



4.1.3 Other Factors Affecting Tributary Mercury Concentrations

As previously mentioned (see Section 4.1.2), peaks in mercury concentrations in some tributaries coincided with either spring high flow conditions or high flows related to storm events. Significant positive correlations existed between flow and total mercury concentrations (both log transformed) in six tributaries (the Fox, Grand, Sheboygan, Milwaukee, Menominee, and Manistique Rivers). In these six tributaries, r^2 values indicated that flow accounted for 17 to 65% of the variability in total mercury concentrations (Table 4-4). For methylmercury, only two tributaries (the Fox and Menominee Rivers) exhibited significant positive correlations with flow.

Table 4-4. Correlation of Tributary Mercury Levels with Tributary Flow

Fraction	Tributary	N	Correlation Coefficient	r^2	p-value
Total Mercury	Fox	38	0.417	0.174	0.0091
	Grand	45	0.431	0.185	0.0032
	Grand Calumet	13	0.311	0.0965	0.302
	Kalamazoo	37	-0.0729	0.00532	0.668
	Manistique	25	0.806	0.649	<0.0001
	Menominee	24	0.662	0.438	0.0004
	Milwaukee	36	0.656	0.430	<0.0001
	Muskegon	26	0.258	0.0666	0.203
	Pere Marquette	26	0.271	0.0732	0.181
	Sheboygan	34	0.595	0.354	0.0002
	St. Joseph	32	0.136	0.0185	0.458
Total Methylmercury	Fox	15	0.579	0.335	0.0238
	Grand	31	-0.00648	0.0000410	0.972
	Grand Calumet	7	-0.0705	0.00497	0.881
	Kalamazoo	14	-0.313	0.0980	0.276
	Manistique	21	0.344	0.118	0.127
	Menominee	12	0.589	0.347	0.0440
	Milwaukee	21	0.357	0.128	0.112
	Muskegon	11	-0.273	0.0743	0.418
	Pere Marquette	19	-0.227	0.0517	0.349
	Sheboygan	32	0.310	0.0963	0.0838
	St. Joseph	16	0.285	0.0811	0.285

Because most of the mercury in the water column is bound to dissolved or suspended organic matter (USEPA, 1997c), mercury concentrations are expected to correlate with measures of solids and organic carbon. In coordination with tributary sampling of mercury, samples also were analyzed for dissolved organic carbon (DOC), particulate organic carbon (POC), and total solids (TS). Four of the eleven tributaries showed significant positive correlations between total mercury and DOC concentrations (Table 4-5). Seven tributaries showed significant positive correlations between total mercury and POC concentrations. In these seven tributaries, POC accounted for 23 to 62% of the variability in total mercury concentrations. The strongest correlations, however, were between TS and total mercury concentrations. All but the Muskegon River exhibited significant positive correlations between TS and total mercury. Total solids accounted for up to 82% of the variability in total mercury concentrations. It is possible that the POC and DOC correlations were auto-correlations, due to the attachment of not only mercury, but also POC and DOC, to the total solids.

Table 4-5. Correlations of Total Mercury Levels in Lake Michigan Tributaries with Dissolved Organic Matter (DOC), Particulate Organic Matter (POC), and Total Solids (TS)

Analyte	Tributary	N	Correlation Coefficient	r^2	p-value
DOC	Fox	38	-0.221	0.0488	0.182
	Grand	42	0.341	0.116	0.0273
	Grand Calumet	15	0.463	0.215	0.0820
	Kalamazoo	34	0.221	0.0488	0.209
	Manistique	24	0.531	0.282	0.0076
	Menominee	22	0.281	0.0791	0.205
	Milwaukee	34	0.511	0.261	0.0020
	Muskegon	26	-0.192	0.0368	0.348
	Pere Marquette	26	0.259	0.0670	0.202
	Sheboygan	33	0.676	0.457	<0.0001
	St. Joseph	31	-0.116	0.0134	0.536
POC	Fox	37	0.625	0.391	<0.0001
	Grand	42	0.220	0.0483	0.162
	Grand Calumet	13	0.776	0.602	0.0018
	Kalamazoo	33	0.0805	0.00648	0.656
	Manistique	25	0.347	0.120	0.0896
	Menoninee	23	0.500	0.250	0.0151
	Milwaukee	34	0.638	0.407	<0.0001
	Muskegon	25	-0.0868	0.00753	0.680
	Pere Marquette	26	0.651	0.424	0.0003
	Sheboygan	29	0.790	0.624	<0.0001
	St. Joseph	30	0.476	0.227	0.0078
TS	Fox	38	0.786	0.618	<0.0001
	Grand	45	0.606	0.367	<0.0001
	Grand Calumet	14	0.855	0.731	<0.0001
	Kalamazoo	36	0.817	0.668	<0.0001
	Manistique	25	0.663	0.439	0.0003
	Menominee	24	0.832	0.693	<0.0001
	Milwaukee	35	0.881	0.777	<0.0001
	Muskegon	25	-0.215	0.0464	0.301
	Pere Marquette	26	0.823	0.677	<0.0001
	Sheboygan	32	0.908	0.824	<0.0001
	St. Joseph	31	0.775	0.600	<0.0001

4.1.4 Mercury Forms

Total and dissolved fractions of mercury were directly measured in the LMMB Study, and mercury in the particulate fraction was calculated by subtraction. Tributaries varied greatly in the contribution of mercury from the dissolved and particulate fractions. Tributaries ranged from the Muskegon River, with the impact of Lake Muskegon, where virtually all of the total mercury (99%) was attributable to the

dissolved fraction, to the Grand Calumet River, where virtually all of the total mercury (92%) was attributable to the particulate fraction (Table 4-6). There was a distinct separation of tributaries that were dominated by the dissolved mercury fraction and tributaries that were dominated by the particulate mercury fraction. The Menominee, Manistique, Pere Marquette, and Muskegon Rivers were dominated by the dissolved mercury fraction. Each of these tributaries contained greater than 50% of total mercury in the dissolved fraction, and the Manistique, Pere Marquette, and Muskegon Rivers contained greater than 75% of total mercury in the dissolved fraction. These tributaries are the more northern tributaries with more forested watersheds.

The Fox, Grand Calumet, and Kalamazoo Rivers were dominated by mercury in the particulate fraction. Each of these tributaries contained more than 75% of total mercury in the particulate fraction. These three tributaries are among the most urbanized and industrialized watersheds evaluated in the study.

In addition to measurement of total and dissolved mercury, methylmercury was measured in the total and dissolved fractions. In most of the tributaries, methylmercury comprised less than 6% of the total mercury (Table 4-6). This is consistent with USEPA (1997c) reports that less than 10% of total mercury in a water column typically exists as a methylmercury complex. The one exception was the Muskegon River, where methylmercury accounted for an average of 21% of total mercury. As Hurley *et al.* (1998b) explained, Lake Muskegon is located directly upstream of the Muskegon River sampling site. This lake traps particulates and particulate-bound contaminants, which reduces the load of particulate mercury in the Muskegon River. As evidence of this, the Muskegon River had the lowest particulate mercury concentration (virtually zero), the lowest particulate organic carbon concentration (0.537 mg/L), and the lowest total solids concentration (3.04 mg/L). In addition to reducing the particulate load of mercury, Lake Muskegon could provide favorable conditions for the methylation of mercury. This could explain the much higher percentage of methylmercury in the Muskegon River than other tributaries.

Methylmercury is the bioavailable form of mercury that is readily accumulated and biomagnified in aquatic food webs. While methylmercury accounts for less than 10% of the total mercury in surface waters, methylmercury typically accounts for more than 90% of total mercury in fish tissue (Watras and Bloom, 1992).

Table 4-6. Percentages of Total Mercury Found in Various Forms

Tributary	Mean Percent of Total Mercury as [a]		
	Dissolved	Particulate	Methylmercury
Fox	15	85	0.97
Grand Calumet	8	92	0.48
Grand	43	57	2.6
Kalamazoo	19	81	2.0
Manistique	78	22	4.7
Menominee	54	46	5.3
Milwaukee	34	66	5.2
Muskegon	99	0.64	21
Pere Marquette	80	20	5.6
Sheboygan	38	62	5.9
St. Joseph	29	71	2.1

[a] The dissolved and particulate fractions are mutually exclusive and add to 100% of the total mercury. The percent of total mercury in the form of methylmercury is presented separately, however, this portion may exist in either dissolved or particulate fractions as well and is already accounted for in those fractions.

4.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of tributary mercury and methylmercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Tables 4-7 and 4-8 provide a summary of flags applied to the tributary mercury and methylmercury data, respectively. The summaries include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. A total of 15 dissolved mercury and 15 total mercury samples were flagged as invalid by the PI. These samples were invalidated because they were prepared and analyzed without a Tenax TA® pretrap (see section 3.19 of USEPA 1997b) and data quality was significantly reduced. These samples were not used in any of the statistical analyses described in this report. For methylmercury, no samples were flagged invalid, and therefore, all results were used in the statistical analyses described in this chapter.

Table 4-7. Summary of Routine Field Sample Flags Applied to Mercury Data from Lake Michigan Tributaries

Flag	Number of QC samples		Percentage of Samples Flagged	
	Dissolved	Total	Dissolved	Total
INV, Invalid Result	—	—	4% (15)	4% (15)
EHT, Exceeded Holding Time	—	—	0	0
FDL, Failed Lab Duplicate	340 lab duplicate groups	347 lab duplicate groups	4% (15)	2% (6)
FFD, Failed Field Duplicate	49 field duplicate pairs	49 field duplicate pairs	3% (9)	3% (11)
FSL, Failed Lab Fortified Spike	65 lab fortified spike samples	53 lab fortified spike samples	1% (3)	1% (2)

The most frequently applied data validation flag for methylmercury data was for exceeding sample holding times. More than half of the samples analyzed for methylmercury (55% of dissolved methylmercury, and 57% of total methylmercury samples) were analyzed beyond the 2-year established

holding time. The median holding time for methylmercury samples was 1,358 days, and samples were held as long as 1,897 days prior to methylmercury analysis. The MQOs for holding times were based on educated, conservative assessments by the PIs, however, the appropriateness of these holding times have not been rigorously determined and the effects of extended holding times have not been investigated in the tributary matrix. All total and dissolved mercury samples were analyzed within the 2-year holding time, and therefore, no total or dissolved mercury results were flagged for exceeding the holding time.

Table 4-8. Summary of Routine Field Sample Flags Applied to Methylmercury Data from Lake Michigan Tributaries

Flag	Number of QC samples		Percentage of Samples Flagged	
	Dissolved	Total	Dissolved	Total
INV, Invalid Result	—	—	0	0
EHT, Exceeded Holding Time	—	—	55% (113)	57% (117)
FDL, Failed Lab Duplicate	14 lab duplicate pairs	11 lab duplicate pairs	3% (6)	0.5% (1)
FFD, Failed Field Duplicate	28 field duplicate groups	30 field duplicate groups	10% (21)	9% (18)
FSL, Failed Lab Fortified Spike	19 lab fortified spike samples	25 lab fortified spike samples	16% (33)	19% (38)

Field blanks were analyzed to assess the potential for contamination of routine field samples. For total and dissolved mercury, a total of 36 blanks were analyzed, including 12 field reagent blanks, 12 field tubing blanks and 12 field filter blanks. Two field tubing blanks and one field reagent blank contained greater than 1 ng/L mercury and were flagged as contaminated according to the established MQOs. The maximum mercury concentration in these blanks was 1.2 ng/L. In addition, one other field reagent blank and associated field filter blank were flagged because the difference between these two blank concentrations and their associated field tubing blank was greater than 0.50 ng/L. In total, 14% of the blanks were flagged for contamination. However, because the blanks could not be associated with individual field samples, no field samples were flagged for blank failures. For methylmercury, no blank contamination flags were applied to the field samples. One field trip blank sample was analyzed, with a concentration of -0.0050 ng/L. Negative values are possible for methylmercury due to the analytical methodology, which involves the subtraction of results from two analytical steps.

Field and laboratory duplicate samples were analyzed to assess the precision of the measurement system. A total of 88 and 60 valid field duplicate samples were analyzed for mercury and methylmercury, respectively, including 2 cases where a methylmercury field sample had multiple duplicates. All field duplicate samples were classified as "sequential" because the duplicates were not collected within five minutes of the original sample due to equipment mobilization and sample pumping time. At least three sequential field duplicates were collected from each tributary for total and dissolved mercury analysis. For methylmercury analysis, at least one sequential field duplicate was collected from every tributary except for the Fox River. In accordance with the researcher's data qualifying rules for field duplicates, total and dissolved mercury samples were flagged for a failed field duplicate (FFD) based on a maximum relative percent difference (RPD) of 30% for samples greater than 5 times the method detection limit (MDL) and 50% for samples less than 5 times the MDL. A total of 9 dissolved mercury samples and 11 total mercury samples exceeded these maximum RPD limits. For methylmercury, a maximum RPD limit of 30% was used if all results were above 0.10 ng/L (approximately 5 times the MDL), and an absolute difference of 0.030 ng/L was used if at least one result was below 0.10 ng/L. These criteria were exceeded for 39 field duplicate pairs, however, only 8 of these pairs failed using the RPD criterion. The

remaining 31 pairs failed based on the absolute difference criterion, with the maximum absolute difference between duplicates equaling 1.1 ng/L.

For total and dissolved mercury analysis, at least one laboratory duplicate was prepared for all but 19 field samples. For some samples, multiple laboratory duplicates (up to 4) were prepared. Laboratory duplicates also were prepared for several field duplicate samples. For methylmercury analysis, laboratory duplicates were prepared for only 25 field samples, with no more than one laboratory duplicate prepared for a given sample. In accordance with the researcher's data qualifying rules for lab duplicates, total and dissolved mercury samples were flagged for a failed duplicate (FDL) based on a maximum RPD level (or RSD if more than one lab duplicate was analyzed for a given sample) of 20% for samples greater than 5 times the MDL and 50% for samples less than 5 times the MDL. A total of 15 dissolved and 6 total mercury sample pairs exceeded these maximum RPD/RSD criteria, with a maximum RPD/RSD of 80% calculated. For methylmercury, the rules for determining lab duplicate failure were the same as those used for determining field duplicate failure. These criteria were exceeded for 7 laboratory duplicate pairs. Three of these pairs failed using the RPD criterion and 4 pairs failed based on the absolute difference criterion. The maximum RPD measured for methylmercury samples was 107%, and the maximum absolute difference (between field sample and duplicate) was 0.34 ng/L.

To monitor the potential bias of analytical results, the laboratory prepared and analyzed a total of 162 laboratory fortified spike samples (LSFs). Samples were flagged for a failed lab fortified spiked sample (FSL) if the associated spike recovery was below 70% or above 130%. The FSL flag was applied to 1% of the total and dissolved mercury samples, due to two recoveries below the lower limit, with a minimum of 66%, and three recoveries above the upper limit, with a maximum of 159%. The FSL flag was applied to 16% of dissolved methylmercury and 19% of total methylmercury samples, due to one recovery below the lower limit (69%) and four above the upper limit, with a maximum of 153%. Based on analysis of laboratory spikes, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the field sample and duplicate result for laboratory duplicate pairs. Tables 4-9 and 4-10 provide summaries of data quality assessments for several of these attributes for tributary mercury and methylmercury data, respectively. The results of laboratory and field duplicate samples revealed good system and analytical precision for total and dissolved mercury data when the results were above 5 times the given MDL. System precision was described by mean RPDs of 17% and 20% for dissolved and total field duplicate samples, respectively. Analytical precision was even greater, with RPDs as low as 7.5% and 5.1% for dissolved and total mercury samples, respectively. When results were less than 5 times the MDL, mean RPDs were much higher. For field duplicates, the mean RPD was 45% for the 7 dissolved duplicate pairs and 182% for the one total duplicate pair. For laboratory duplicates, the mean RPDs were 14% for dissolved mercury samples and 54% for total mercury samples.

Methylmercury results were less precise than total and dissolved mercury results. For results that were greater than 5 times the MDL, mean field duplicate RPDs were 47% for dissolved methylmercury and 27% for total methylmercury. Mean laboratory duplicate RPDs were 47% and 13% for dissolved and total methylmercury, respectively, when all results were above 5 times the MDL. When results were less than 5 times the MDL, mean field duplicate RPDs were 99% and 51% for dissolved and total methylmercury, respectively. Mean laboratory duplicate RPDs were 62% and 26% for dissolved and total methylmercury, respectively.

Analytical bias was evaluated by calculating the mean recovery of LSF samples. Results indicated very little overall bias for analytical results. The mean LSF recovery for total and dissolved mercury was 103%. For methylmercury, the mean LSF recovery for dissolved samples was 99%, and the mean LSF recovery for total methylmercury was 110%.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the corresponding MDL (0.10 ng/L for total and dissolved mercury, and 0.019 ng/L for total and dissolved methylmercury). Only one dissolved mercury sample, or 0.3% of the data, and no total mercury samples, were below the detection limit for total mercury. For methylmercury, 31 dissolved samples (15% of the data) and 6 total samples (3% of the data) were below the MDL. Results from these samples were not censored and were used as reported in the analysis of tributary mercury data presented in this report.

Table 4-9. Data Quality Assessment for Mercury Data from Lake Michigan Tributaries

Parameter	Assessment[a]	
	Dissolved	Total
Number of Routine Samples Analyzed	346	353
Number of Sequential Field Duplicates Analyzed	49	49
System Precision, Mean Field Duplicate RPD (%), < 5*MDL	45% (7)	182% (1)
System Precision, Mean Field Duplicate RPD (%), > 5*MDL	17% (34)	20% (46)
Analytical Precision, Mean Lab Duplicate RPD (%), < 5*MDL	14% (29)[b]	54% (1)[b]
Analytical Precision, Mean Lab Duplicate RPD (%), > 5*MDL	7.5% (338)[b]	5.1% (381)[b]
Analytical Bias, Mean LFS (%)	103% (65)	103% (53)
Analytical Sensitivity, Samples reported as < MDL (%)	0%	0%

[a] Number of QC samples used in the assessment is provided in parentheses
[b] Includes laboratory duplicates of field duplicate samples
LFS = Laboratory Fortified Spike
MDL = Method Detection Limit

Table 4-10. Data Quality Assessment for Methylmercury Data from Lake Michigan Tributaries

Parameter	Assessment[a]	
	Dissolved	Total
Number of Routine Samples Analyzed	204	203
Number of Sequential Field Duplicate Groups Analyzed	28	30
System Precision, Mean Field Duplicate RPD (%), < MDL	99% (22)	51% (17)
System Precision, Mean Field Duplicate RPD (%), > MDL	47% (3)	27% (12)
Analytical Precision, Mean Lab Duplicate RPD (%), < MDL	62% (9)	26% (3)
Analytical Precision, Mean Lab Duplicate RPD (%), > MDL	47% (4)	13% (8)
Analytical Bias, Mean LFS (%)	99% (19)	110% (25)
Analytical Sensitivity, Samples reported as < MDL (%)	15%	3%

[a] Number of QC samples used in the assessment is provided in parentheses
LFS = Laboratory Fortified Spike
MDL = Method Detection Limit

4.3 Data Interpretation

4.3.1 Mercury Levels in Lake Michigan Tributaries

Total mercury concentrations in Lake Michigan tributaries averaged from 1.07 ng/L in the Muskegon River to 28.9 ng/L in the Fox River. Following the Fox River, the Kalamazoo and Grand Calumet Rivers averaged approximately 10 ng/L in total mercury. The remaining tributaries averaged from 1 to 6 ng/L in total mercury. These mercury levels are comparable to mercury concentrations measured in other Midwestern tributaries. In a survey of 39 Wisconsin rivers, Hurley *et al.* (1995) measured a mean total mercury concentration of 7.94 ng/L during the spring and 3.45 ng/L during the fall. This is consistent with LMMB Study data, where a majority of tributaries averaged between 3 and 7 ng/L total mercury. Similarly, Thompson-Roberts *et al.* (1999), measured average total mercury concentrations of 3 to 19 ng/L in 23 wetlands of the St. Lawrence River. Balogh *et al.* (1998) reported total mercury concentrations below 4 ng/L in the St. Croix River, below 10 ng/L in the headwaters of the Mississippi River, and routinely above 10 ng/L in the Minnesota River. In a summary of surface water mercury levels nationwide, USEPA (1997c) reported that total mercury levels in lakes and streams are typically well under 20 ng/L, however, elevated levels may be found in lakes and streams thought to be impacted by anthropogenic mercury sources. This is consistent with the results of this study, where all tributaries except for the Fox River were below 20 ng/L, and the Fox River is suspected of being impacted by resuspension of contaminated sediments from legacy sources (Hurley *et al.*, 1998a).

4.3.2 Comparison to Regulatory Limits

The average concentrations of mercury in Lake Michigan tributaries were all below EPA's nationwide freshwater water quality criterion for human health protection of 50 ng/L, and only the Fox River exceeded the chronic water quality criterion for protection of aquatic life (12 ng/L). When compared to the more stringent water quality criteria recommended for Great Lakes states, three tributaries exceed the Great Lakes water quality criterion for human health (1.8 ng/L dissolved mercury) and eight tributaries exceed the Great Lakes water quality criterion for wildlife (1.3 ng/L dissolved mercury). The Fox, Manistique, and Menominee Rivers exceed the human health criterion, and all tributaries except for the Muskegon, Milwaukee, and Grand Calumet Rivers exceed the wildlife criterion.

4.3.3 Seasonality

While tributaries differed in their seasonal patterns of flow and mercury concentrations, many of the Lake Michigan tributaries exhibited significantly lower mercury concentrations during the winter and higher mercury concentrations in conjunction with spring high-flow conditions or event flows during the summer and fall. Balogh *et al.* (1998) similarly found that total mercury concentrations in the Minnesota, St. Croix, and Mississippi Rivers varied seasonally with lowest levels during the winter, increasing concentrations during spring runoff, and fluctuating concentrations throughout the spring, summer, and fall in response to precipitation runoff events. In the Minnesota River, Balogh *et al.* (1997) reported total mercury concentrations from less than 1.0 ng/L during the winter months to greater than 35 ng/L following spring runoff. When comparing just spring and fall concentrations, Hurley *et al.* (1995) found strong seasonal variability in 39 Wisconsin Rivers, with total mercury concentrations approximately two times higher in the spring than in the fall.

In tributaries that are dominated by particulate mercury, lower total mercury concentrations during the winter are tied to lower suspended solids concentrations during the winter. The low-flow conditions that occur during the winter in conjunction with the ice cover that forms over many Lake Michigan tributaries contribute to reduced turbulence and reduced sediment resuspension. This reduced suspended sediment load during the winter decreases particulate, and therefore total, mercury concentrations in the water

column (Hurley *et al.*, 1998a). This conclusion is consistent with correlations of total mercury with particulate organic carbon concentrations, total solids concentrations, and suspended particulate matter identified in this and other studies (Hurley *et al.*, 1998a; Balogh *et al.*, 1998; Balogh *et al.*, 1997).

Seasonal differences in the fluxes of mercury from Lake Michigan tributaries were even more apparent than seasonal differences in mercury concentrations alone. Hurley *et al.* (1998b) investigated the fluxes of mercury from Lake Michigan tributaries during three flow regimes: spring, base flow, and event. For all tributaries except the Grand Calumet, base flow fluxes were considerably lower than fluxes during either spring or event conditions. In comparing spring and event fluxes, Hurley *et al.* (1998b) found that the patterns of mercury flux and flow regimes differed among the tributaries. In the Fox, St. Joseph, and Manistique Rivers, fluxes associated with the spring flows were much greater than those associated with summer and fall events. In contrast, mercury fluxes in the Grand and Kalamazoo Rivers were greater during summer and fall events than during spring flows. These differences were explained in part by differences in watershed land use patterns (Hurley *et al.*, 1998b). The Grand and Kalamazoo River watersheds contain significant agricultural land cover with increased particulate erosion susceptibility during precipitation events.

4.3.4 Regional Considerations

Of the 11 Lake Michigan tributaries evaluated in the LMMB Study, total mercury concentrations were highest in the Fox River. Average total mercury concentrations in the Fox River were 2.7 times higher than in any other tributary. The maximum total mercury concentration of 191 ng/L measured in the Fox River was more than four times higher than the maximum concentration measured in any other tributary. Following the Fox River, total mercury concentrations were highest in the Grand Calumet and Kalamazoo Rivers. Total mercury concentrations in these two rivers were significantly higher than in any other tributary, except for the Fox River. Each of these rivers (the Fox, Grand Calumet, and Kalamazoo) have significantly urbanized and industrialized watersheds, which suggests anthropogenic sources. In more intensive surveys of the lower Fox River that included longitudinal transect sampling and analysis of sediment cores, Hurley *et al.* (1998a) concluded that mercury enrichment in the Fox River was due to resuspension of historically contaminated sediments. Mercury concentrations of up to 5.69 µg/g in deeper sediment cores (18-cm composites) in conjunction with scouring from high flow events were sufficient to produce the water column mercury levels measured at the mouth of the Fox River. Hurley *et al.* (1998b) also measured mercury levels in the suspended particulate matter on a ng/g basis and concluded that the Fox and Grand Calumet Rivers contained particles that were highly enriched with mercury compared to the other tributaries. Levels of mercury in particles from the remaining tributaries were generally 50 to 200 ng/g and in the range reported for Midwestern soils.

While the highest total mercury concentrations were observed in urban and industrial watersheds, the lowest total mercury concentrations were observed in predominantly forested and wetland watersheds. The more-northern Muskegon, Manistique, Pere Marquette, and Menominee Rivers contained the lowest total mercury concentrations, averaging only 1.07 to 3.63 ng/L. Hurley *et al.* (1995) also found that mercury yields varied by watershed land use patterns in 39 Wisconsin rivers. Mean spring concentrations and yields of mercury were highest in urban watersheds, followed by wetland and forest watershed, with lowest values in agricultural watersheds.

4.3.5 Mercury Fractions and Forms

Tributaries also differed in the fractions and forms of mercury present. In each of the three most mercury-contaminated tributaries (Fox, Grand Calumet, and Kalamazoo Rivers), mercury was predominantly in the particulate fraction. Particulate mercury accounted for 85%, 92%, and 81% of total mercury in the Fox, Grand Calumet, and Kalamazoo Rivers, respectively. In the least contaminated

tributaries (the Muskegon, Manistique, Pere Marquette, and Menominee Rivers), total mercury concentrations were dominated by the dissolved fraction. The dissolved fraction accounted for 54% to 99% of total mercury in these tributaries. In fact, the Manistique, Menominee, and Pere Marquette Rivers contained the second, third, and fourth highest average dissolved mercury concentrations. Hurley *et al.* (1998b), however, notes that on a flux basis, inputs of dissolved mercury from the Fox, Kalamazoo, Grand, and St. Joseph Rivers are of the same magnitude as those from the dissolved mercury-dominated tributaries.

Balogh *et al.* (1998) found similar results when investigating mercury in diverse Minnesota river basins. In the more forested and wetland-dominated watershed of the St. Croix River, the dissolved fraction dominated mercury mobility, while the particulate fraction dominated mercury mobility in the agricultural Minnesota River watershed. Dissolved mercury accounted for over 62% of the total mercury in the St. Croix River and less than 10% of the total mercury in the Minnesota River. Likewise, wetland/forest watersheds in Wisconsin were dominated by mercury fluxes in the filtered fraction, while agricultural watersheds were dominated by mercury fluxes in the particulate fraction (Hurley *et al.*, 1995).

With the exception of the Muskegon River (where methylmercury accounted for 21% of total mercury), methylmercury accounted for only 0.48% to 5.9% of total mercury in Lake Michigan tributaries. In a study of 39 Wisconsin rivers, Hurley *et al.* (1995) similarly found that methylmercury accounted for an average of less than 2.2% to 6.4% of total mercury. Lake Michigan tributaries such as the Fox, Grand Calumet, and Kalamazoo Rivers that had the highest total mercury concentrations did not have correspondingly high methylmercury concentrations. These tributaries ranked fifth, sixth, and tenth in total methylmercury concentrations among the tributaries. Hurley *et al.* (1998b) cautioned, however, that just because those sites with high total mercury levels contained only a small portion of mercury in more bioavailable dissolved and methyl forms, these loads should not be discounted as inert. These particulate-bound contaminants can be deposited in Lake Michigan sediments and undergo methylation, reintroducing biologically available mercury to the Lake Michigan system.

Chapter 5
Mercury in the Open-Lake Water Column

Open-lake water column samples were collected during six cruises of the *R/V Lake Guardian* conducted from April 1, 1994 to October 22, 1995. Samples were collected at 17 sampling locations, including 15 stations in Lake Michigan, 1 location in Green Bay and 1 location in Lake Huron (see Figure 2-4). Samples were collected at depths ranging from 1 m to 150 m. Samples were collected as described in Section 2.4.3 and analyzed for total and particulate mercury by cold-vapor atomic fluorescence spectrometry (see Section 2.5.3). In addition, dissolved mercury results were calculated by subtracting the particulate mercury result from the total mercury result, when results from both fractions were reported.

5.1 Results

A total of 121 samples were analyzed for particulate mercury, and a total of 125 samples were analyzed for total mercury (Table 5-1). Particulate mercury results ranged from 0.027 ng/L to 0.30 ng/L, with approximately 8% of the samples below the associated daily detection limit. Total mercury results ranged from 0.037 ng/L to 0.78 ng/L, with approximately 4% of the samples below the associated daily detection limit. Combining data from all depths and all cruises, the lake-wide mean mercury concentrations measured in this study were 0.33 ng/L for total mercury and 0.11 ng/L for particulate mercury.

Table 5-1. Numbers of Open-Lake Samples Analyzed for Mercury

Sampling Station	Sampling Dates	Particulate Samples	Total Mercury Samples	Total Number of Samples
GB24M	08/08/94 to 09/20/95	7	7	14
LH54M	08/03/94 to 09/16/95	10	10	20
05	08/24/94 to 10/10/95	8	8	16
140	06/18/94 to 09/23/95	8	8	16
180	04/07/95 to 04/07/95	1	1	2
18M	06/22/94 to 10/09/95	12[a]	12	24
23M	06/23/94 to 10/03/95	12	12	24
240	06/21/94 to 10/02/95	7	9	16
27M	06/20/94 to 09/27/95	10	10	20
280	04/01/95 to 04/01/95	1	1	2
340	08/21/94 to 10/06/95	7	7	14
380	03/26/95 to 03/26/95	1	1	2
40M	10/18/94 to 09/25/95	7	8	15
41	06/18/94 to 10/22/94	4	5	9
47M	06/17/94 to 09/19/95	12	12	24
19M	08/19/94 to 10/05/95	8	8	16
72M	08/04/94 to 09/17/95	6	6	12
	Total	121	125	246

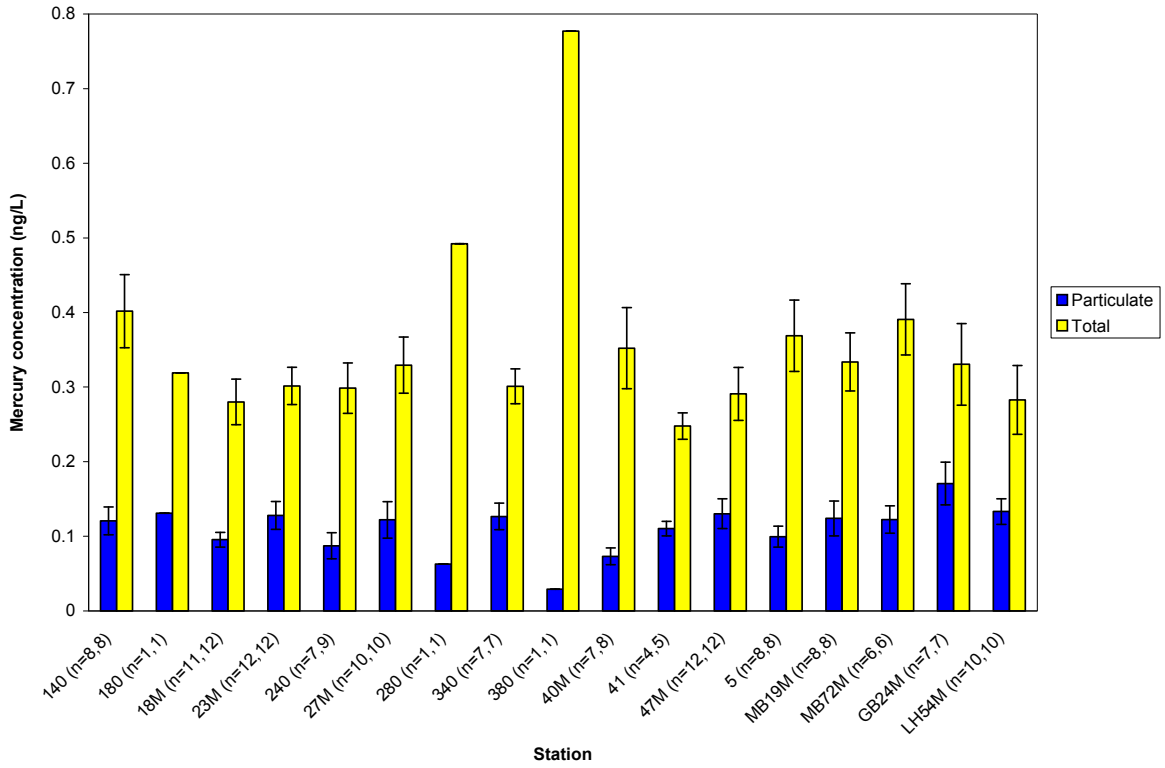
[a] One sample was invalid.
GB = Green Bay station
LH = Lake Huron station

5.1.1 Geographical Variation

From 1 to 12 samples were collected at each of 17 different stations in Lake Michigan, Green Bay, and Lake Huron. The mean concentrations are shown in Figure 5-1, and descriptive statistics of the particulate and total mercury concentrations reported at each station are presented in Table 5-2. Mean particulate mercury concentrations ranged from 0.029 ng/L at Station 380 to 0.17 ng/L at Station GB24M in Green Bay. The maximum mean particulate mercury concentration in Lake Michigan was 0.13 ng/L, and occurred at five different stations. Mean total mercury concentrations ranged from 0.25 ng/L at Station 41 to 0.78 ng/L at Station 380. While the mean particulate and total mercury concentrations collected at Station 380 were extremely low and high, respectively, compared to the other stations, these means only represent a single sample result at this station. Therefore, it is unlikely that these means are representative of the mercury concentrations at that station.

The highest mean particulate mercury value was in Green Bay (GB24M). This finding is not unexpected, due to the large inputs of mercury, particularly in the particulate phase, from the Fox River (see Chapter 4). While particulate mercury concentrations were slightly higher in Green Bay than other sampling sites, there were no significant differences among site in particulate mercury concentrations, based on a one-way Analysis of Variance (ANOVA) model using log-transformed results (p=0.1685). Mean total mercury concentrations were relatively consistent throughout Lake Michigan. No statistical differences were observed among sampling sites, based on a one-way ANOVA model using log-transformed results (p=0.2309).

Figure 5-1. Mercury Concentrations Measured in Open-lake Water Column Samples



Stations are from Lake Michigan except for GB24M (Green Bay) and LH54M (Lake Huron). Bars show the mean mercury concentration of samples collected at each station for the duration of the study. Error bars are standard error.

Table 5-2. Mean Particulate and Total Mercury Concentrations Measured in Open Lakes

Fraction	Sampling Station	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Particulate	140	8	0.12	0.12	0.049 to 0.19	0.053	44	13
	180	1	0.13	0.13	NA	NA	NA	0.0
	18M	11	0.095	0.094	0.030 to 0.15	0.033	35	0.0
	23M	12	0.13	0.11	0.031 to 0.24	0.065	51	0.0
	240	7	0.087	0.063	0.038 to 0.16	0.046	53	14
	27M	10	0.12	0.12	0.030 to 0.30	0.077	63	10
	280	1	0.063	0.063	NA	NA	NA	0.0
	340	7	0.13	0.13	0.05 to 0.19	0.047	37	0.0
	380	1	0.029	0.029	NA	NA	NA	0.0
	40M	7	0.073	0.073	0.038 to 0.11	0.029	40	0.0
	41	4	0.11	0.10	0.097 to 0.14	0.020	18	0.0
	47M	12	0.13	0.13	0.035 to 0.28	0.070	53	17
	5	8	0.10	0.10	0.032 to 0.15	0.040	40	25
	GB24M	7	0.17	0.19	0.076 to 0.30	0.076	45	14
	LH54M	10	0.13	0.12	0.079 to 0.27	0.054	41	20
	19M	8	0.12	0.13	0.027 to 0.20	0.066	53	0.0
	72M	6	0.12	0.13	0.057 to 0.17	0.045	36	0.0
Total	140	8	0.40	0.42	0.21 to 0.61	0.14	35	0.0
	180	1	0.32	0.32	NA	NA	NA	0.0
	18M	12	0.28	0.27	0.14 to 0.46	0.11	38	8.3
	23M	12	0.30	0.30	0.21 to 0.48	0.086	29	8.3
	240	9	0.30	0.27	0.19 to 0.48	0.10	34	0.0
	27M	10	0.33	0.28	0.22 to 0.57	0.12	36	0.0
	280	1	0.49	0.49	NA	NA	NA	0.0
	340	7	0.30	0.30	0.22 to 0.39	0.062	21	0.0
	380	1	0.78	0.78	NA	NA	NA	0.0
	40M	8	0.35	0.30	0.19 to 0.57	0.15	44	13
	41	5	0.25	0.25	0.19 to 0.30	0.040	16	0.0
	47M	12	0.29	0.28	0.075 to 0.48	0.12	42	8.3
	5	8	0.37	0.33	0.19 to 0.55	0.14	37	0.0
	GB24M	7	0.33	0.29	0.16 to 0.56	0.14	44	0.0
	LH54M	10	0.28	0.34	0.037 to 0.49	0.15	52	10
	19M	8	0.33	0.30	0.20 to 0.54	0.11	33	0.0
	72M	6	0.39	0.34	0.30 to 0.59	0.12	30	0.0

NA = Not applicable
GB = Green Bay station
LH = Lake Huron station

Statistical comparisons also were performed after combining the 15 stations in Lake Michigan into two different basins. For these comparisons, the data from the LMMB Study were divided at approximately 44° north latitude. The dividing line at 44° N is not intended as a formal differentiation between hydrographic basins in the lake, and other means of differentiating the results from north to south could be considered. The latitude limit was instead chosen to remain consistent with analyses performed on PCB and atrazine data. The results from the stations in Green Bay and Lake Huron were excluded from these comparisons. Based on the 44° N dividing line, six of the 15 Lake Michigan stations were categorized as being in the northern basin (40M, 41, 47M, 72M, 140 and 180).

The results of the basin comparisons were similar to those of the comparisons of individual stations. For both particulate and total mercury, there were no significant differences in mercury concentration between basins (particulate: $p = 0.1046$; total: $p = 0.2523$) or between stations nested within basin (particulate: $p = 0.3869$; total: $p = 0.0805$).

The lack of spatial differences is consistent with previous assessments that suggest that the primary source of mercury is atmospheric rather than riverine (Mason and Sullivan, 1997). The effect of the variability in mercury concentration among the tributaries, as discussed in Chapter 4, is only seen in the slightly greater particulate mercury concentration in Green Bay at station GB24M. However, the total mercury concentration at this station did not exhibit any effect of the Fox River, as the mean concentration of 0.30 ng/L was below the overall mean total mercury concentration. Therefore, it is likely that most of the mercury from the Fox River is removed to the sediment rather than staying in the water column (Sullivan and Mason, 1998).

5.1.2 Seasonal Variation

Samples were collected during six cruises: June 1994, August 1994, October/November 1994, March/April 1995, August 1995 and September/October 1995. During each cruise, up to 2 samples were collected at each station. Descriptive statistics for particulate and total mercury for each cruise are presented in Table 5-3.

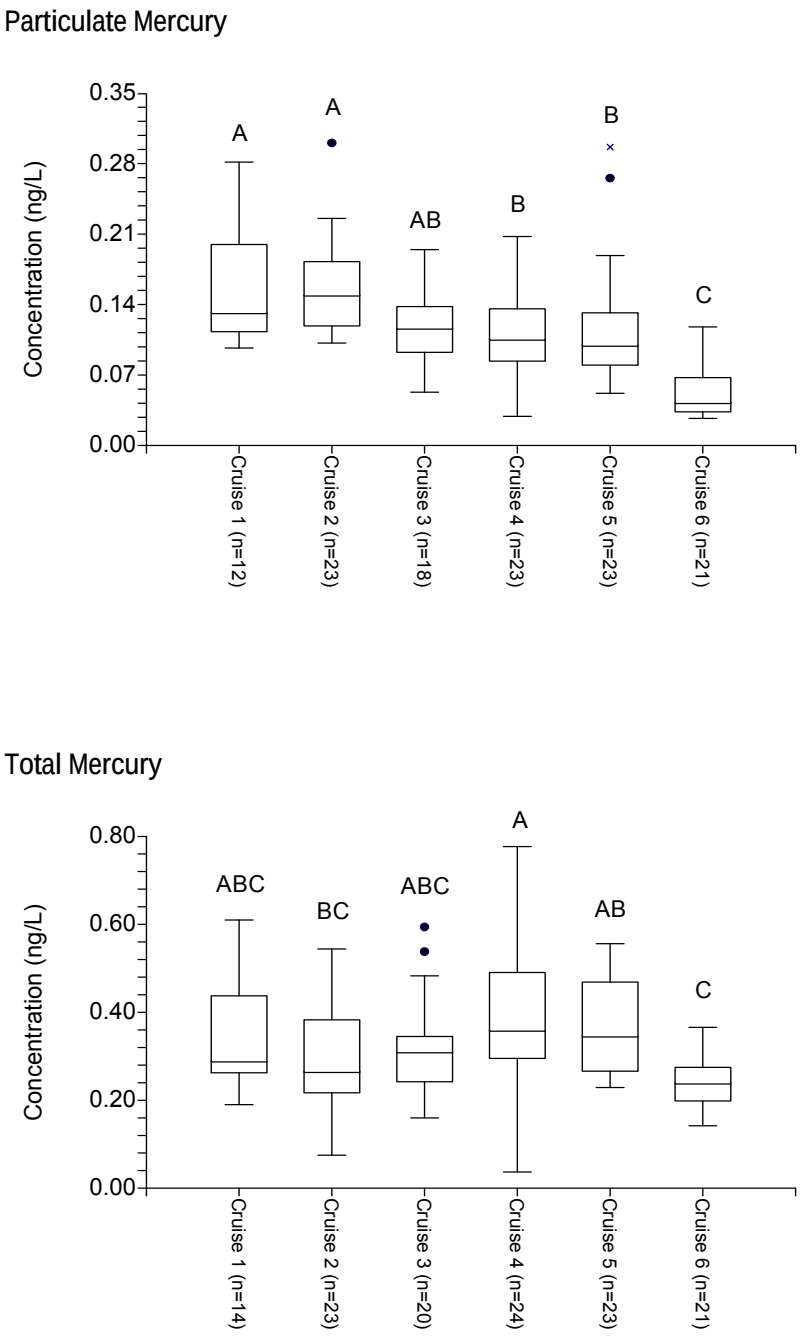
Table 5-3. Mean Particulate and Total Mercury Concentrations by Cruise

Fraction	Sampling Cruise	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Particulate	June 1994	12	0.16	0.13	0.097 to 0.28	0.060	37	0.0
	August 1994	23	0.16	0.15	0.10 to 0.30	0.047	30	43
	Oct./Nov. 1994	18	0.12	0.12	0.053 to 0.20	0.039	32	0.0
	March/April 1995	23	0.11	0.11	0.029 to 0.21	0.040	37	0.0
	August 1995	23	0.12	0.10	0.052 to 0.30	0.062	53	0.0
	Sept./Oct. 1995	21	0.052	0.043	0.027 to 0.12	0.024	46	0.0
Total	June 1994	14	0.34	0.29	0.19 to 0.61	0.12	35	0.0
	August 1994	23	0.29	0.27	0.075 to 0.54	0.12	41	13
	Oct./Nov. 1994	20	0.33	0.31	0.16 to 0.59	0.12	36	0.0
	March/April 1995	24	0.38	0.36	0.037 to 0.78	0.16	41	8.3
	August 1995	23	0.36	0.35	0.23 to 0.56	0.10	29	0.0
	Sept./Oct. 1995	21	0.24	0.24	0.14 to 0.37	0.062	26	0.0

Mean particulate mercury concentrations generally decreased over the course of the study, ranging from 0.16 ng/L in the June and August 1994 cruises to 0.052 ng/L in the autumn 1995 cruise. Based on a one-way ANOVA model, the difference between cruises was significant ($p<0.0001$). Subsequent Tukey pairwise comparisons showed that the means for the first two cruises were significantly greater than the means for the last three cruises, and that the mean of the last cruise was significantly lower than the means for all other cruises (Figure 5-2A). Unlike particulate mercury, mean total mercury concentrations did not appear to follow a trend. The maximum mean total mercury concentration occurred in March/April 1995, rather than in summer 1994. However, similar to particulate mercury, the minimum concentration occurred in September/October 1995. A one-way ANOVA model comparing mean total mercury concentrations between cruises was statistically significant ($p = 0.0015$). Tukey pairwise comparisons showed that the means of the March/April and August 1995 cruises were significantly greater than the mean for the September/October 1995 cruise and that the mean of the March/April cruise was significantly greater than the mean of the August 1994 cruise (Figure 5-2B).

Because the timing of the cruises differed between the two years of collection, it is difficult to interpret the concentration differences between cruises as seasonal or annual differences. Cruises 2 and 5 occurred during August, however, and differences could be interpreted as due to differences between 1994 and 1995. Based on profiles of temperature and pH, Sullivan and Mason (1998) concluded that productivity in the lake was lower in the summer of 1994 compared to the summer of 1995. They hypothesize that the increase in pH from August 1995 to September/October 1995 is evidence of the pH-induced precipitation of calcite, a mineral form of calcium carbonate, and they conclude that the seasonal dynamics of the lake differed between the two years of the LMMB Study. These differences in dynamics may have an effect on the concentrations and partitioning of mercury in the lake.

Figure 5-2. Particulate and Total Mercury Concentrations Measured in Open Lakes, by Cruise



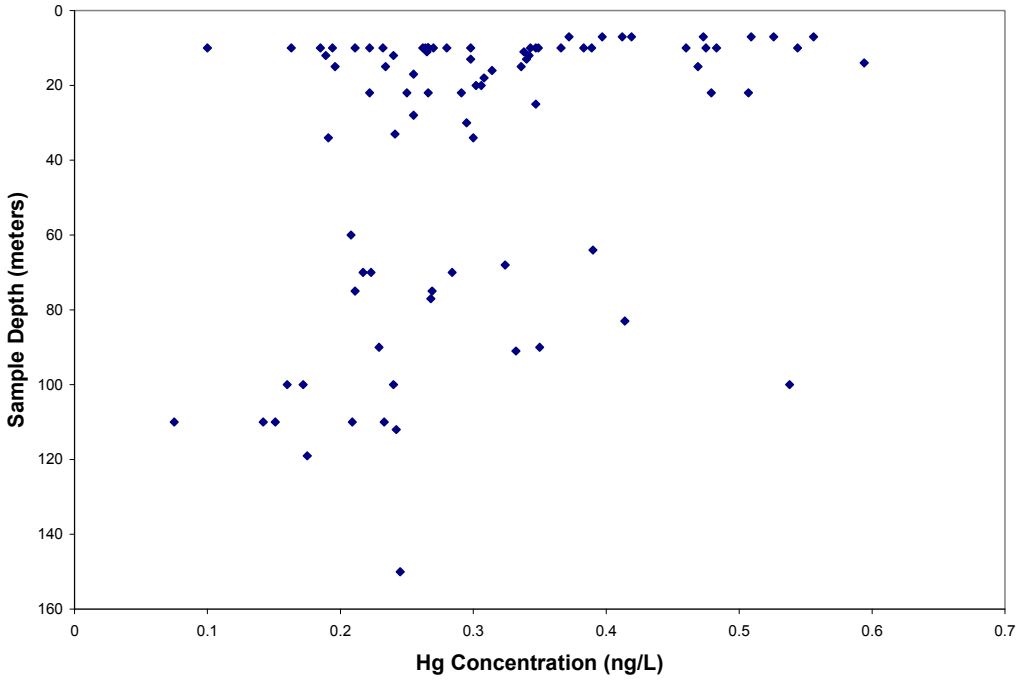
Cruise 1 = June 1994, Cruise 2 = August 1994, Cruise 3 = September/October 1994, Cruise 4 = March/April 1995, Cruise 5 = August 1995, and Cruise 6 = September/October 1995

Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

5.1.3 Vertical Variation

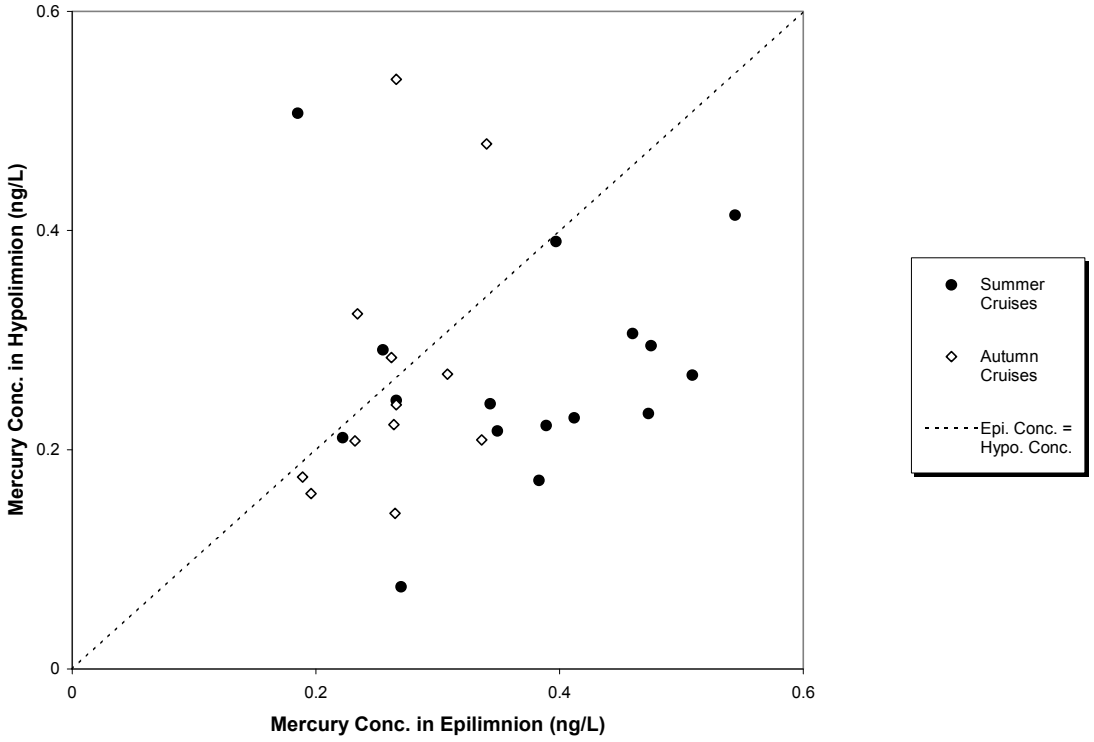
Open-lake samples were collected at depths ranging from 1 to 150 m. The correlation between sampling depth and mercury concentration (both log-transformed) was weak for particulate (r^2 = 0.057) mercury, and did not differ significantly from 0 (p = 0.539). The correlation between depth and concentration for total mercury (r^2 = -0.203) was also somewhat weak, but differed significantly from 0 (p = 0.0235). The overall weak correlation between depth and concentration may be due to station variability and variability among cruises conducted during completely mixed or thermally stratified conditions. If correlations are calculated based on only the samples collected during stratified conditions, (i.e., cruises during late summer and autumn months), the negative correlation for total mercury strengthens (r^2 = -0.393, p = 0.0002), while the particulate mercury correlation remains weak (r^2 = 0.047, p = 0.666). The correlation is presented graphically in Figure 5-3. While the relationship does not appear strong, concentrations collected at depths above (shallower than) 40 meters were significantly greater than those collected below 40 meters, based on a two-sample *t*-test (p = 0.0008).

Figure 5-3. Total Mercury Concentration versus Sample Depth During Stratified Conditions



To further account for station and cruise variability, a paired *t*-test was used to compare the mercury concentration at the deeper depth (hypolimnion) to the concentration at the shallower depth (epilimnion) where samples were collected at two depths for a given cruise and station. Two sample pairs for which both depths were either above 20 meters or below 20 meters were not included in the analyses, leaving 27 pairs for particulate mercury and 28 pairs for total mercury. These pairs were collected either during a late summer cruise (August 1994, August 1995) or an autumn cruise (October/November 1994, September/October 1995). When tests were conducted separately by these seasonal categories, there was a significant difference between the two depths for total mercury during the late summer (p = 0.0141), where the concentration was greater in the hypolimnion, but not for the autumn (p = 0.7337). These comparisons are shown in Figure 5-4. There were no significant differences between the two depths for either season for particulate mercury (Summer: p = 0.1230, Autumn: p = 0.7867). The lack of a difference between depths during the autumn cruises may be due to a decomposing thermocline late in the fall season (i.e., the end of stratification).

Figure 5-4. Total Mercury Concentrations at Stations with Samples from Multiple Depths



Statistical comparisons were also conducted to compare mercury concentrations for the two seasonal categories defined above separately for the epilimnion and hypolimnion samples. Based on two-sample *t*-tests with the Satterthwaite correction for differences in variability, there was a significant difference in total mercury concentration between the two seasons for the shallower, epilimnion samples (Summer > Autumn, $p<0.004$), but not for the deeper, hypolimnion samples ($p = 0.766$). Therefore, it would appear that the cruise differences discussed in the previous section, (i.e., the low concentrations in the autumn 1995 cruise) were mainly driven by concentration differences in the epilimnion rather than in the hypolimnion. For particulate mercury there was a significant difference for both the epilimnion (Summer>Autumn, $p = 0.010$) and hypolimnion (Summer>Autumn, $p = 0.002$) samples. Therefore, it would appear that the cruise differences in particulate mercury were driven by differences in both stratification levels of the lake.

5.1.4 Mercury Forms

Total and particulate phases of mercury were measured in Lake Michigan during the LMMB Study, and mercury in the dissolved phase was calculated by subtraction. Calculated dissolved mercury concentrations ranged from -0.12 ng/L to 0.75 ng/L. The calculated dissolved mercury concentrations for six samples were negative, including three samples collected at the station in Lake Huron, and three others from different stations collected during the August 1994 cruise. These negative values generally reflect the low concentrations of total mercury in the samples overall, and reflect the analytical uncertainties in both the total and particulate mercury concentrations for the samples. Dissolved mercury concentrations differed significantly by cruise ($p = 0.0077$), but not by station ($p = 0.1730$), based on ANOVA models (results log-transformed when possible prior to analysis). Tukey pairwise comparisons between cruises revealed that the dissolved mercury concentration during March/April 1995 was significantly greater than the concentration during August 1994. Descriptive statistics of calculated dissolved mercury concentrations are presented in Table 5-4 below. The relative standard deviations

(RSDs) for dissolved mercury during each cruise are greater than the RSDs for particulate or total mercury. This is because the dissolved mercury results were calculated, rather than measured, which increases the variability of the results.

Table 5-4. Mean Dissolved Mercury Concentrations by Cruise

Sampling Cruise	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
June 1994	12	0.19	0.16	0.078 to 0.42	0.097	50
August 1994	23	0.13	0.11	-0.12 to 0.36	0.13	100
Oct./Nov. 1994	18	0.21	0.18	0.055 to 0.51	0.14	66
March/April 1995	23	0.28	0.27	-0.076 to 0.75	0.17	62
August 1995	23	0.24	0.24	-0.026 to 0.43	0.13	52
Sept./Oct. 1995	21	0.19	0.19	0.033 to 0.31	0.070	37

In addition, the ratio of particulate to total mercury was calculated for each sample. For five of the six cruises, the mean ratios were below 0.50 (i.e., total mercury concentration more than double the particulate mercury concentration), ranging from 0.24 to 0.46. The only cruise for which this was not true was the August 1994 cruise, which had a mean ratio of 0.68. These differences between the August 1994 cruise and the rest of the data do not appear to be due to seasonality, as seen by the much lower ratios for the August 1995 cruise (mean=0.36).

5.1.5 Other Factors Affecting Tributary Mercury Concentrations

In previous studies, it has been observed that mercury concentration is correlated positively with DOC and negatively with pH (Watras *et al.*, 1995). Samples were analyzed for both DOC and pH during the LMMB Study. However, the samples collected for DOC and pH were not the same samples in which mercury was analyzed. While pH and DOC samples were collected at the same stations during the same day that mercury samples were collected, the sample depths were generally not the same. Therefore, correlations between mercury and DOC and pH could not be calculated. However, if mercury was associated with either pH or DOC, then any spatial or temporal differences observed in mercury may also be observed in the other parameters, either in the same direction (DOC) or opposite direction (pH).

To assess this possible relationship, ANOVA models for the effect of station and cruise were conducted for both pH and DOC. While pH and DOC samples were collected at more stations and cruises than those for which mercury samples were collected, these added samples were not included in the analyses. Based on the ANOVA models, pH did not differ significantly among the 15 Lake Michigan stations for which mercury samples were collected ($p=0.941$), but DOC concentrations did differ significantly among stations ($p=0.0017$; results were log-transformed prior to analysis). Subsequent Tukey pairwise comparisons showed that the DOC levels at Station 72M were significantly lower than for three other stations (180, 280 and 340). However, this was not consistent with the mercury results, as the mean mercury concentration for this station was slightly greater than the overall mean for both the particulate and total fractions. ANOVA comparisons of pH and DOC among cruises showed that mean pH differed significantly among cruises ($p<0.0001$), but mean DOC did not differ significantly ($p = 0.0531$; results were log-transformed prior to analysis). Subsequent Tukey pairwise comparisons showed that pH during the two August cruises was significantly greater than during the spring 1995 and two autumn cruises, and that mean pH during the June 1994 cruise was significantly greater than during the autumn 1994 and spring 1995 cruises. This shows some evidence of an inverse relationship, as total mercury peaked in the spring, while pH was lowest.

5.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of the open-lake mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 5-5 provides a summary of flags applied to the open-lake mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. One particulate mercury result was qualified as invalid due to a suspected leak in the sample, and was not used in the analyses of open-lake mercury concentrations presented in this report.

Table 5-5. Summary of Routine Field Sample Flags Applied to Mercury in Open-lake Samples

Flag	Number of QC samples		Percentage of Samples Flagged (%)	
	Particulate	Total	Particulate	Total
INV, Invalid Result	—	—	0.8% (1)	0
DDL, Below Daily Detection Limit	—	—	8% (10)	4% (5)
EHT, Exceeded Holding Time	—	—	0	0
FDL, Failed Lab Duplicate	45 lab duplicate groups	63 lab duplicate groups	8% (10)	18% (22)
FFD, Failed Field Duplicate	18	18	7% (8)	6% (7)
FFR, Failed Field Blank	13	17	0	0
FPC, Failed Lab Performance Check	114		19% (23)	26% (33)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

Holding time flags were applied based on a criterion of 120 days between sampling and analysis. All data met this criterion, with a maximum lag between sampling and analysis of 115 days.

The analytical sensitivity of field samples was assessed through analysis of daily detection limits. A different limit was calculated for each day of analysis, with a maximum of 12 field samples associated with a given daily detection limit. A "below daily detection limit" flag (DDL) was applied if a given field sample concentration fell below its associated daily detection limit. The DDL flag was applied to 8% of particulate mercury sample results and to 4% of total mercury sample results.

Field reagent blanks were analyzed to assess the potential for contamination of routine field samples. A total of 24 valid field reagent blanks were analyzed, with concentrations ranging from -0.33 ng/L to 0.099 ng/L. In accordance with the researcher's data qualifying rules for field blanks, these blank results were compared to a maximum of 0.10 ng/L. Because this level was never exceeded, no blanks or associated samples were flagged with associated blank failure.

A total of 31 field duplicate samples and 133 laboratory duplicate samples were analyzed to assess precision. The laboratory duplicate samples include both replicate analyses of field samples and field duplicates, with up to 3 duplicates associated with a given field sample. From each cruise (except the January 1995 cruise that visited only two sites), duplicate samples were collected at one to three stations. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD or FDL) if the relative percent difference (RPD) (or relative standard deviation, RSD, where more than one laboratory duplicate was prepared for a given field sample) between results for a sample and its duplicate was greater than 20%. This criterion was not met for 15 field duplicate pairs and for 32 laboratory duplicate groups. The maximum field duplicate RPD was 96%, and the maximum laboratory duplicate RPD/RSD was 109%. While these RPDs were high, they were based on low concentrations which were either below the daily detection limit or only slightly above.

Laboratory performance check samples were used to monitor analytical bias. In accordance with the researcher's data qualifying rules for laboratory performance checks, samples were flagged for a failed performance check (FPC) if the associated concentration was outside the concentration range of 0.80 to 1.2 ng (corresponding to 80% to 120% recovery). Based on application of this criterion, 23% of the field samples were associated with a failed performance check. These flags were applied based on 28 performance check results exceeding 1.2 ng, with a maximum of 1.7 ng. Based on an analysis of laboratory spikes, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD or RSD between the results for laboratory duplicate groups. Table 5-6 provides a summary of data quality assessments for several of these attributes for open-lake data. The mean RPD for field duplicate sample results was 28% for particulate mercury and 21% for total mercury, where both the sample and duplicate results were greater than the daily detection limit. The mean RPD/RSDs for laboratory duplicate samples were 15% and 17% for particulate and total mercury, respectively, where all results were above the daily detection limit.

Analytical bias was evaluated by calculating the mean recovery of laboratory performance check samples (LPC). Results indicated a slight positive bias, with a mean recovery of 110%. This bias applies to both particulate and total mercury, as the LPC samples were not associated with a specific fraction.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the daily detection limit. The mean daily detection limit was 0.063 ng/L, and ranged from 0.010 ng/L to 0.26 ng/L. The majority of field samples were above the corresponding daily detection limit, with only 8% of

particulate mercury sample results and 4% of total mercury sample results falling below the given limit. Results from these samples were not censored and were used as reported in the analysis of open-lake mercury data presented in this report.

Table 5-6. Data Quality Assessment for Mercury in Open-lake Samples

Parameter	Assessment	
	Particulate	Total
Number of Routine Samples Analyzed	121	125
Number of Field Duplicates Analyzed	18	18
System Precision, Mean Field Duplicate RPD (%), <DDL[a]	—	39% (1)
System Precision, Mean Field Duplicate RPD (%), >DDL[a]	28% (16)	21% (13)
Analytical Precision, Mean Lab Duplicate RPD (%), <DDL[a]	11% (1)[b]	60% (3)[b]
Analytical Precision, Mean Lab Duplicate RPD (%), >DDL[a]	15% (47)[b]	17% (68)[b]
Analytical Bias, Mean LPC (percent recovery)	110% (111)	
Analytical Sensitivity, Samples reported as <DDL (%)	8%	4%

[a] Number of Sample/duplicate pairs used in the assessment is provided in parentheses
[b] Includes lab duplicate pairs of field duplicates
DDL = Daily Detection Limit
LPC = Laboratory Performance Check

As previously shown in Table 5-3, all the particulate mercury results that were below the DDL were collected in the August 1994 cruise. However, the mean concentration from that cruise was significantly greater than many of the other cruises. The high number of below DDL results from that cruise is due to a DDL exceeding 0.23 ng/L, run on a day for which samples from this cruise only were analyzed. This was the only DDL exceeding 0.20 ng/L run on days for which particulate samples were analyzed. This high DDL, in addition to the greater particulate mercury concentrations in this cruise, suggests the possibility of slight contamination occurring during the analysis of these samples. In general, the variability of the DDLs was approximately equal to that of the particulate mercury results. The standard deviation of the DDLs was 0.067 ng/L, while the standard deviation of the particulate mercury results was 0.058 ng/L. This is more likely due to the relatively low level of particulate mercury concentrations in Lake Michigan than to any QC issues with the laboratory. However, it is possible that some of the temporal differences observed in the particulate mercury may be partially due to some analytical differences between the analytical batches associated with the different cruises.

5.3 Data Interpretation

5.3.1 Mercury Levels in Lake Michigan

The mean and median total mercury concentrations from the 15 stations located in Lake Michigan were 0.33 ng/L and 0.30 ng/L, respectively. Comparisons of this mean and median to previous studies are complicated by changes in analytical methods and the increased use of clean sampling techniques in recent years. Therefore, there are no historical Lake Michigan data against which to compare the current results.

The mean concentrations from the LMMB Study were below those measured in other lakes using clean sampling techniques and comparable analytical methodology. For example, Watras, *et al.* (1995) measured total mercury and calculated particulate mercury for 23 lakes in Wisconsin in 1993. The mean

total mercury concentration from these lakes was 1.48 ng/L for total mercury and 0.37 ng/L for particulate mercury. Watras and Bloom (1992) also measured total mercury in the lower trophic levels of an acidified basin and a reference basin in Little Rock Lake in Wisconsin in 1990. The mean total mercury concentration in the reference basin was 0.0011 ng/g, or 1.1 ng/L. Mercury concentrations similar to those measured in Lake Michigan were measured in three drainage lakes in Manitoba, with total mercury concentrations ranging from 0.2 to 1.1 ng/L (Bloom and Effler, 1990, based on their personal communication with J.W.M. Rudd).

The differences in mercury concentration between Lake Michigan and the lakes measured in previous studies are not surprising, given the inherent differences between the lakes. In addition to the greater area and depth of Lake Michigan, there are also differences in the chemistry of the lakes. For example, the mean DOC and pH for the LMMB Study were 1.57 mg/L and 8.20, respectively. In contrast, mean DOC concentrations and pH measured in 23 Wisconsin lakes were 6.62 mg/L and 6.17, respectively (Watras *et al.*, 1995). Monson and Brezonik (1998) also reported DOC concentrations in 12 lakes in northeastern Minnesota that were similar to those in the Wisconsin lakes, ranging from 4.5 to 10.2 mg/L, and similar pH levels, ranging from 6.2 to 6.8. In addition, correlations between total mercury and various chemical parameters were reported by Watras *et al.* (1995), with mercury having a strong positive correlation with DOC ($r^2 = 0.93$) and a strong negative correlation with pH ($r^2 = -0.51$). However, these correlations do not necessarily explain the mercury differences between Lake Michigan and the other two studies, as correlations do not necessarily imply a causal relationship.

5.3.2 Comparison to Regulatory Limits

The freshwater water quality criterion established by EPA for human health protection is 50 ng/L for mercury. This is more than an order of magnitude above the mean concentration measured in the lakes in this study (0.33 ng/L). The mean concentration in this study is also less than the criteria for human health (1.8 ng/L) and wildlife (1.3 ng/L) for the Great Lakes states.

5.3.3 Lateral Variation

Neither total mercury nor particulate mercury differed significantly between the 15 stations in Lake Michigan at which samples were collected. This lends support to the theory that the primary source of mercury to Lake Michigan is atmospheric (Sullivan and Mason, 1998), rather than riverine. A larger level of riverine input would have been suggested if stations located closer to tributaries, especially GB24M, had higher levels of mercury. The lack of spatial variability in concentrations in Lake Michigan was also supported by the generally homogeneous levels of pH and DOC in Lake Michigan samples. Only DOC exhibited significant differences between stations, as one northern Lake Michigan station had a lower DOC concentration than three of the other stations.

5.3.4 Temporal Variation

Seasonal patterns in the total and particulate results were not clear, due to differences in the timing of the cruises in the two years of the study. For total mercury, the mean concentration was greatest during the fourth cruise (March/April 1995), and was significantly greater than for two other cruises. This cruise was the only one that occurred during the spring, which suggests that the difference may be due to a seasonal effect. Peak mercury concentrations in lakes during the spring were also observed by Monson and Brezonik (1998) in 12 lakes in Minnesota and by Bloom and Effler (1990) in the Onondaga Lake in New York. However, seasonal patterns during summer and autumn seemed to differ between the two years in the LMMB Study. The September/October 1995 cruise had the lowest mean total mercury concentration and was significantly lower than the other two cruises run in 1995. The October/November 1994 cruise did not exhibit a similar drop in concentration, but in fact, had a mean mercury concentration

slightly greater than the other two 1994 cruises. These differences in patterns may have been partially due to a calcite precipitation event occurring in 1995 (Sullivan and Mason, 1998). A drop in mercury concentration has not generally been observed in prior studies. Monson and Brezonik (1998), in fact, observed an increase in concentration in autumn compared to summer. The lower concentration in autumn 1995 is also unexpected, based on the lower productivity level in 1994 (Sullivan and Mason, 1998).

Unlike total mercury, particulate mercury concentrations did not peak during the spring, instead they were greatest in the June 1994 and August 1994 cruises. Similar to total mercury, the lowest concentrations were observed during the September/October cruise. These results were not consistent with the productivity level differences in the two years. It is worth noting that the August 1994 cruise had greater daily detection limit values than the other cruises. Based on the low levels and variability of concentrations measured in this study, any differences could have been strongly affected by slight levels of contamination.

Seasonal differences were also affected by lake stratification. The four late summer and autumn cruises included samples from multiple depths at most stations, representing the epilimnion and hypolimnion levels of the lake. For total mercury, the concentrations in the epilimnion were significantly greater in the summer compared to the autumn.

While mercury concentrations differed by cruise, DOC concentrations did not. This was unexpected, given the strong positive correlations observed between DOC and total mercury in past studies. Mean pH did differ significantly between cruises, with peak levels occurring during summer, and lower levels occurring during the spring and autumn.

5.3.5 Vertical Variation

Total and particulate mercury concentrations were generally higher at depths closer to the surface, though the effect of depth on concentration was not strong. Higher concentrations were expected near the surface, because atmospheric deposition is considered to be the primary source of mercury input (Sullivan and Mason, 1998). This effect of depth was greater during the late summer cruises, i.e., during peak stratification conditions. The timing of the two autumn cruises differed, as the autumn 1994 cruise began in mid-October, whereas the autumn 1995 cruise began in mid-September. However, there were not enough pairs collected during these two cruises to assess the effect the timing difference had on stratification of mercury.

Samples analyzed for total mercury were also collected at different depths and seasons from Lake Onondaga in New York (Bloom and Effler, 1990). Similar to the current study, differences in concentration between surface and hypolimnion depths (measured at 18 m) were greatest during the summer. However, the direction of the difference was not the same, as the total mercury concentration was greater in the hypolimnion. Similar to the current study, the difference between depths was minimal in autumn. Total mercury concentrations in the hypolimnion also exceeded concentrations in the epilimnion in Devil's Lake in Wisconsin (Herrin, *et al.*, 1998). While epilimnion concentrations were similar to those observed in this study (ranging from 0.10 to 1.0 ng/L), hypolimnion concentrations were as high as 2.0 ng/L.

A possible difference between the relationship between depth and concentration in Lake Michigan and in the other lakes is the greater depth of Lake Michigan. The maximum depths of Lake Onondaga and Devil's Lake are 20.5 m and 14 m, respectively. The depths of the Lake Michigan stations from which mercury samples were collected ranged from 27 m to 259 m. This difference could have played a role in the relationship between depth and mercury concentration. For smaller, shallower lakes, the role of

sediment resuspension, compared to atmospheric input, will likely be greater than for larger, deeper lakes. This increased role of sediment resuspension would result in a greater level of mercury in the hypolimnion compared to the surface of the lake.

5.3.6 Mercury Fractions and Forms

For five of the six cruises, the majority of the total mercury was in the dissolved, rather than particulate, phase. This result is similar to that observed by Watras *et al.* (1995) in 23 Wisconsin lakes. However, Bloom and Effler (1990) found that the majority of total mercury was in the particulate fraction in Lake Onondaga. In addition, Bloom and Effler observed that the percentage of total mercury in the particulate fraction was greatest in the autumn. The authors hypothesized that this was due to the coagulation of suspended matter after lake turnover.

Chapter 6
Mercury in Surficial Sediments

6.1 Introduction

6.1.1 Background

Sediments can be a reservoir of trace contaminants. This is true for mercury, which is strongly attached to particles in the water column and settles to the lake bottom along with the particles to become the building blocks of the sediment. Surficial sediment particles enriched in mercury may be resuspended by currents and waves and transported by currents to new locations. Eventually a particle with its associated mercury is buried by particles deposited at a later date. Once the particle ceases to physically interact with the water column, it becomes a part of the permanent sediment record.

From the standpoint of mass balance modeling, those particles that can be resuspended and transported elsewhere within the lake are of interest. Contaminants associated with these particles are subject to transport, creating a flux of materials from one location in the lake to another location in the lake. These surficial sediment particles are also subject to interactions with the food chain, resulting in contaminant exposures to organisms.

6.1.2 Study Objectives

With respect to mercury in sediments, the LMMB Study was designed to describe the horizontal variability of mercury in the surficial sediments of Lake Michigan (Figure 6-1). By agreement among principal investigators of the sediment, surficial sediments were defined as the surficial 1 cm of sediment. Based upon experience, it was decided that this was the depth of sediment most likely available for resuspension. To ascertain the character of resuspended sediments, sediment trap samples were also collected at a number of locations in the lake (Figure 6-2). The locations were to be representative of depositional and non-depositional locations. The specific objectives of the sediment mercury study were to:

- Document concentrations of mercury in surficial sediments,
- Describe the horizontal variation of mercury in surficial sediments,
- Estimate the flux of mercury to the surficial sediments,
- Describe the horizontal variation in mercury fluxes to the surficial sediments, and
- Define the concentration of mercury and its time variation in resuspended sediments.

For Lake Michigan Mass Balance modeling and project objectives, the reader is referred to the modeling and project plans (USEPA, 1995c and 1995d).

Figure 6-1. Sampling Locations and Type of Sample Recovered between 1994 and 1996

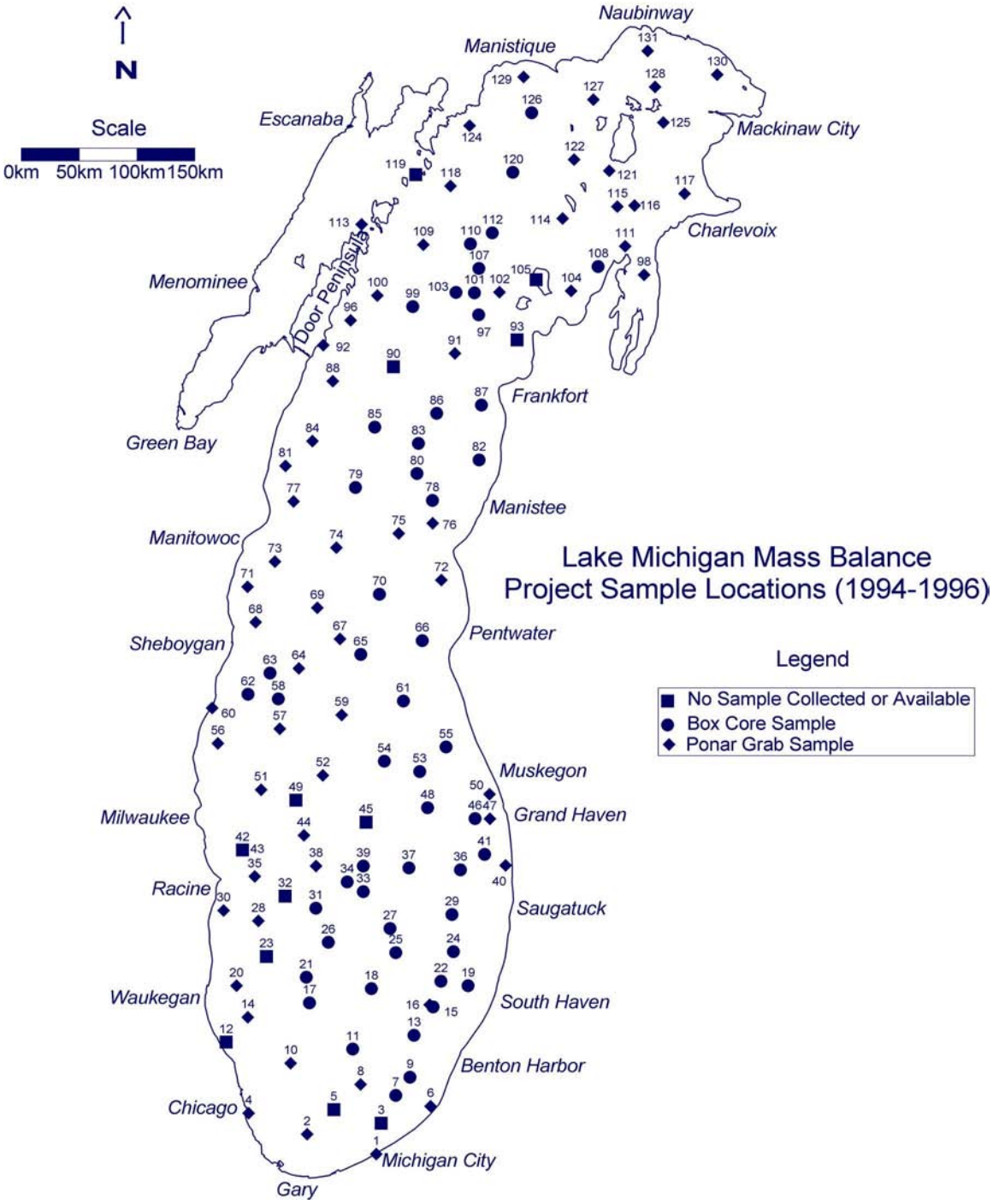
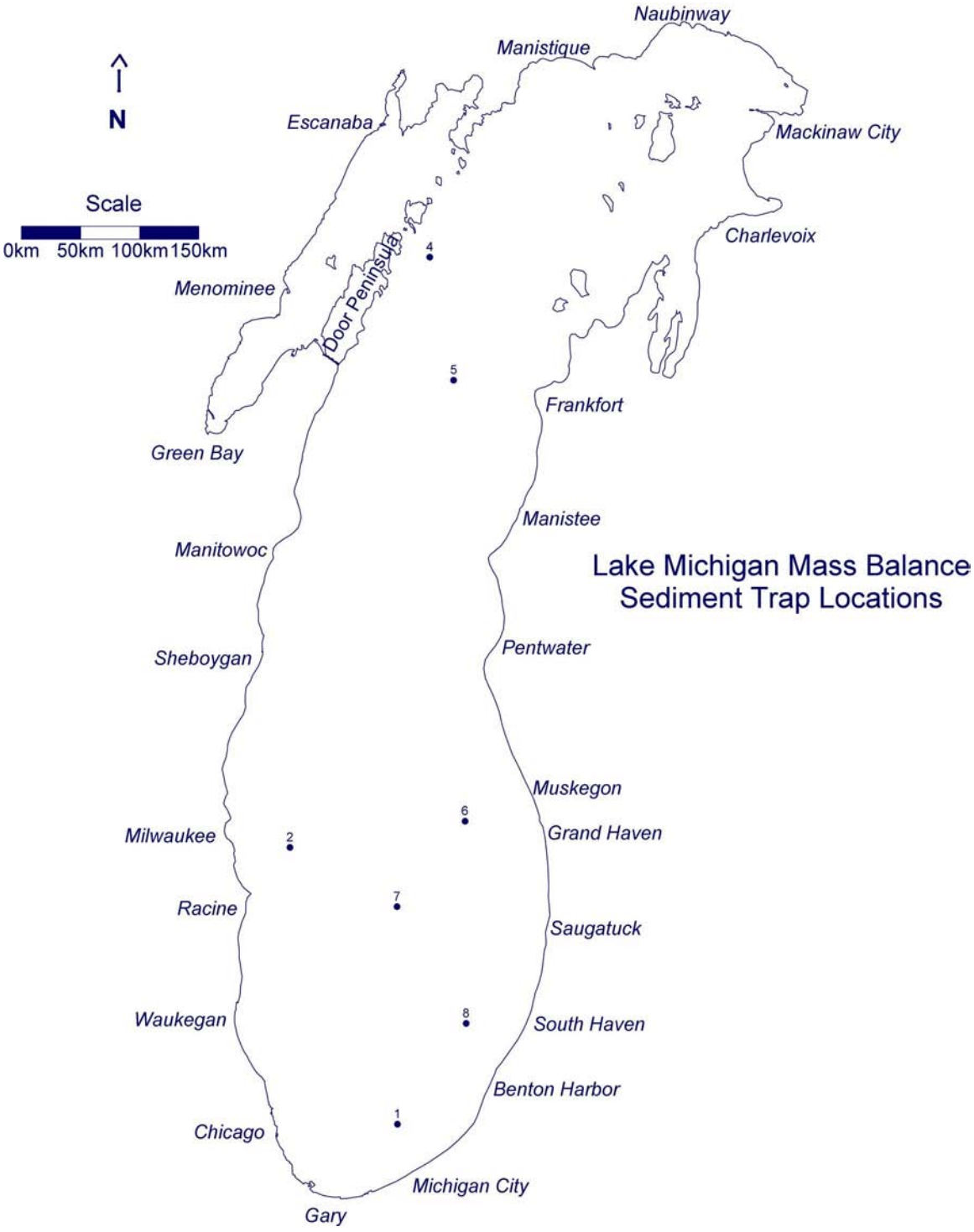


Figure 6-2. Sediment Trap Locations



6.2 Results

6.2.1 Mercury in Surficial Sediments

Surficial sediments were collected using the box corer and Ponar grab sampling techniques (Section 2.4.4). From July 18, 1994 to May 22, 1996, at least one surficial sediment sample was collected at each of 118 stations, for a total of 126 samples (Table 6-1). (Note: The station numbers used for the sediment sample collection effort do not correspond to the station identifiers used for the open-lake water samples described in Chapter 5).

At six stations, both a Ponar grab sample and box core sample were collected; and at another single station, one Ponar grab sample and two box core samples were collected. When more than one sample was collected at a given station using both the Ponar grab and box core devices, the result from the box core sample was used in the data analysis provided in this report because box-coring was the preferred sampling method (see Section 2.4.4). The mean mercury concentration in Lake Michigan surficial sediments was 0.078 mg/kg and the median value was similar (0.079 mg/kg) (Table 6-2).

Table 6-1. Concentrations of Mercury for each Lake Michigan Surficial Sediment Station

Station Number*	Hg Concentration (mg/kg)	LMMB Sample Number
1	0.018	sd1p
2	0.0074	sd2p
4	0.033	sd4p
6	0.006	sd6p
7	0.072	942356
8	0.074	sd8p
9	0.092	942321
10	0.021	sd10p
11	0.040	sd11p
13	0.10	940532
14	0.012	sd14p
15	0.10	940608
16	0.096	sd16p
17	0.14	284
18	0.12	940659
19	0.088	940152
20	0.020	sd20p
21	0.24	940285
22	0.13	940590
24	0.15	940011
25	0.13	943564
26	0.11	951475
27	0.15	940143
28	0.032	sd28p
29	0.17	940102
30	0.036	sd30p

Table 6-1. Concentrations of Mercury for each Lake Michigan Surficial Sediment Station

Station Number*	Hg Concentration (mg/kg)	LMMB Sample Number
31	0.11	950164
33	0.12	943117
34	0.19	951426
35	0.011	sd35p
36	0.14	941861
37	0.10	941802
38	0.11	sd38p
39	0.22	942545
40	0.003	sd40p
41	0.15	943106
43	0.011	sd43p
44	0.050	sd44p
46	0.14	942472
47	0.032	sd47p
48	0.14	942412
50	0.016	sd50p
51	0.018	sd51p
52	0.019	sd52p
53	0.15	942190
54	0.12	942959
55	0.15	941965
56	0.012	sd56p
57	0.084	sd57p
58	0.13	950648
59	0.036	sd59p
60	0.006	sd60p
61	0.17	951452
62	0.11	941233
63	0.14	951795
64	0.10	sd64p
65	0.14	942019
66	0.17	950451
67	0.049	sd67p
68	0.006	sd68p
69	0.013	sd69p
70	0.16	950461
71	0.008	sd71p
72	0.012	sd72p
73	0.022	sd73p
74	0.016	sd74p
75	0.086	sd75p

Table 6-1. Concentrations of Mercury for each Lake Michigan Surficial Sediment Station

Station Number*	Hg Concentration (mg/kg)	LMMB Sample Number
76	0.13	sd76p
77	0.012	sd77p
78	0.14	952700
79	0.15	941148
80	0.12	940829
81	0.020	sd81p
82	0.14	940402
83	0.18	951686
84	0.034	sd84p
85	0.15	951283
86	0.14	951271
87	0.14	940399
88	0.034	sd88p
89	0.028	sd89p
91	0.14	sd91p
92	0.006	sd92p
95	0.26	sd95p
96	0.0045	sd96p
97	0.15	951877
98	0.012	sd98p
99	0.13	950097
100	0.007	sd100p
101	0.13	951858
102	0.029	sd102p
103	0.12	943042
104	0.008	sd104p
106	0.011	sd106p
107	0.12	951823
108	0.16	950698
109	0.004	sd109p
110	0.10	952550
111	0.005	sd111p
112	0.14	952533
113	0.15	sd113p
114	0.034	sd114p
115	0.023	sd115p
116	0.006	sd116p
117	0.026	sd117p
118	0.007	sd118p
120	0.11	952569
121	0.011	sd121p

Table 6-1. Concentrations of Mercury for each Lake Michigan Surficial Sediment Station

Station Number*	Hg Concentration (mg/kg)	LMMB Sample Number
122	0.012	sd122p
123	0.006	sd123p
124	0.004	sd124p
125	0.002	sd125p
126	0.15	950880
127	0.006	sd127p
128	0.012	sd128p
129	0.002	sd129p
130	0.016	sd130p
131	0.041	sd131p

* The station numbers used for the sediment sample collection effort do not correspond to the station identifiers used for the open-lake water samples described in Chapter 5.

Table 6-2. Summary Statistics for Lake Michigan Surficial Sediment Mercury Concentrations

Descriptive Statistic	Result
Mean Concentration (mg/kg)	0.078
Standard Deviation of Mean (mg/kg)	0.065
Median Concentration (mg/kg)	0.079
Minimum Concentration (mg/kg)	0.002
Maximum Concentration (mg/kg)	0.260
Number of Observations	118

To visually display the results, all data were contoured using a linear variogram with no drift kriging. In order to contour mercury concentrations in surficial sediments, it was necessary to assign a concentration to the boundary of the lake as well as to locations from which sediment samples could not be recovered. This boundary concentration was set at 0.0035 mg/kg, the average mercury concentration measured in sand that was relatively free of silt- and clay-sized particles. For contouring fluxes, the net mercury flux chosen for the boundary was 1.2 ng/cm^2/y (Rossmann 1999, Rossmann and Edgington 2000), the estimated regional atmospheric flux of mercury. Without other processes operative, this would be the flux to locations along the shoreline. While these assumptions are oversimplifications (especially in areas impacted by local high fluxes of mercury), the selected boundary conditions represent the most reasonable values that can be obtained without additional data.

6.2.2 Mercury in Sediment Trap Samples

Resuspended sediments were collected using sediment traps (Section 2.3.4). A total of 65 samples from 7 different traps, representing 5 stations, were analyzed for total mercury. Sixteen trap samples from one station having two traps could not be analyzed due to the use of mercury chloride as a preservative. Results for each trap are contained in Table 6-3. (Note: The station numbers used for the sediment trap sample collection effort do not correspond to the station identifiers used for either the sediment core samples in Table 6-1 or the open-lake water samples described in Chapter 5). Approximately 50% of all results had a mercury concentration <0.5 mg/kg. Mercury concentrations at 30 m water depth were highest at Station 7 and were lowest at Station 5 (Table 6-4).

Table 6-3. Concentrations of Mercury in Sediment Trap Samples

Station Number*	Trap Number	Sequence Number	Trap Water Depth (m)	Sample Number	Mercury Concentration (mg/kg)
7	5	2	30	ST314	27
7	5	9	30	ST321	6.1
7	5	10	30	ST322	4.2
7	5	11	30	ST323	4.8
7	5	12	30	ST324	2.9
7	5	15	30	ST327	3.9
7	5	16	30	ST328	2.2
7	5	17	30	ST329	5.8
7	5	18	30	ST330	6.9
7	5	23	30	ST335	11.
7	4	2	155	ST337	1.6
7	4	3	155	ST338	3.0
7	4	4	155	ST339	2.4
7	4	5	155	ST340	2.0
7	4	6	155	ST341	0.95
7	4	7	155	ST342	3.0
7	4	8	155	ST343	1.8
7	4	9	155	ST344	1.1
7	4	10	155	ST345	0.47
7	4	11	155	ST346	0.47
7	4	12	155	ST347	0.38
7	4	13	155	ST348	0.42
7	4	14	155	ST349	0.43
7	4	15	155	ST350	0.40
7	4	16	155	ST351	0.33
7	4	17	155	ST352	0.44
7	4	18	155	ST353	0.66
7	4	19	155	ST354	0.51
7	4	23	155	ST358	1.4
8	7	1	30	ST359	1.1
8	7	2	30	ST360	0.30
8	7	3	30	ST361	0.37
8	7	4	30	ST362	0.36
8	7	5	30	ST363	0.21
8	7	9	30	ST367	0.66
8	7	10	30	ST368	0.91
8	7	11	30	ST369	0.55
8	7	12	30	ST370	0.32
8	7	13	30	ST371	0.43
8	7	14	30	ST372	1.2
8	7	15	30	ST373	2.5

Table 6-3. Concentrations of Mercury in Sediment Trap Samples

Station Number*	Trap Number	Sequence Number	Trap Water Depth (m)	Sample Number	Mercury Concentration (mg/kg)
8	7	16	30	ST374	0.44
8	7	18	30	ST376	1.2
8	7	20	30	ST378	0.64
8	7	21	30	ST379	2.5
8	7	23	30	ST381	1.2
2	9	1	77	ST382	0.30
2	9	7	77	ST385	0.71
8	6	1	51	ST388	0.39
8	6	2	51	ST389	0.61
8	6	3	51	ST390	0.42
8	6	4	51	ST391	0.27
1	8	1	45	ST395	0.31
1	8	2	45	ST396	0.44
5	3	3	30	ST469	0.79
5	3	4	30	ST470	0.42
5	3	10	30	ST476	0.53
5	3	11	30	ST477	0.24
5	3	12	30	ST478	0.27
5	3	13	30	ST479	0.22
5	3	14	30	ST480	0.22
5	3	15	30	ST481	0.25
5	3	16	30	ST482	0.55
5	3	17	30	ST483	0.84
5	3	18	30	ST484	0.43

* The station numbers used for the sediment trap sample collection effort do not correspond to the station identifiers used for either the sediment core samples in Table 6-1 or the open-lake water samples described in Chapter 5.

Table 6-4. Mercury Summary Statistics for each Station at each Depth for Sediment Trap Samples

Station	Depth (m)	Number of Samples	Mean (mg/kg)	Standard Deviation (mg/kg)	Median (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
1	45	2	0.37	NA	0.37	0.31	0.44
2	77	2	0.51	NA	0.51	0.30	0.71
5	30	11	0.43	0.23	0.42	0.22	0.84
7	30	10	7.5	7.4	5.3	2.2	27
7	155	19	1.1	0.90	0.66	0.33	3.0
8	30	17	0.87	0.69	0.64	0.21	2.5
8	51	4	0.42	0.14	0.40	0.27	0.61

It should be noted that the mass of sediment collected from the traps was often too small to complete all analyses targeted in the LMMB Study. Samples were collected and analyzed for mercury only in those cases where the amount of material available in trap samples was sufficient, and this generally

corresponded with periods of high sediment fluxes. Because of these shortcomings in the data set at this time, the authors do not wish to interpret the sediment trap any further.

6.2.3 Moisture Content of Sediment Samples Collected by Ponar

The moisture content ([wet weight - dry weight]/[dry weight] x 100) was measured on each Ponar sample received (Table 6-5). Ponar samples were collected not only from those regions with bottoms too hard to core, but also from areas inaccessible to the ship. Most of these areas were very sandy. A few were very silty sands.

Table 6-5. Moisture Content of Samples Collected by Ponar

Station Number*	LMMB Sample Number	Moisture Content (%)
1	sd1p	25
2	sd2p	22
4	sd4p	24
6	sd6p	22
8	sd8p	70
9	sd9p	67
10	sd10p	31
11	sd11p	53
13	sd13p	76
14	sd14p	32
16	sd16p	43
19	sd19p	88
20	sd20p	30
28	sd28p	44
30	sd30p	53
35	sd35p	26
36	sd36p	75
38	sd38p	65
40	sd40p	22
43	sd43p	24
44	sd44p	52
47	sd47p	40
50	sd50p	28
50	sd50p	23
51	sd51p	42
52	sd52p	44
56	sd56p	32
57	sd57p	52
59	sd59p	52
60	sd60p	23
64	sd64p	74
67	sd67p	52
68	sd68p	27
69	sd69p	31

Table 6-5. Moisture Content of Samples Collected by Ponar

Station Number*	LMMB Sample Number	Moisture Content (%)
71	sd71p	26
72	sd72p	23
72	sd72p	22
73	sd73p	47
74	sd74p	42
75	sd75p	64
76	sd76p	74
77	sd77p	28
81	sd81p	23
84	sd84p	54
88	sd88p	27
89	sd89p	32
91	sd91p	78
92	sd92p	20
95	sd95p	63
96	sd96p	23
98	sd98p	24
98	sd98p	27
100	sd100p	22
102	sd102p	36
104	sd104p	25
106	sd106p	27
109	sd109p	22
111	sd111p	25
111	sd111p	23
113	sd113p	90
114	sd114p	26
115	sd115p	37
116	sd116p	30
117	sd117p	69
118	sd118p	22
121	sd121p	20
122	sd122p	27
123	sd123p	24
124	sd124p	21
125	sd125p	24
127	sd127p	38
128	sd128p	34
129	sd129p	18
130	sd130p	33
131	sd131p	68

* The station numbers used for the Ponar sample collection effort do not correspond to the station identifiers used for the open-lake water samples described in Chapter 5.

Because these data are only for Ponar samples collected from primarily sandy areas, the mean and median moisture contents are relatively low compared to silt- and clay-rich sediments (Table 6-6). The minimum of 18% moisture represents a fairly pure sand, while the maximum of 90% moisture represents a very silt- or clay-rich sand that might even be classified as a silt or clay.

Table 6-6. Summary Statistics for Moisture Content Analyses of Samples Collected by Ponar

Descriptive Statistic	Result
Mean Moisture Content (%)	39
Standard Deviation of Moisture Content (%)	19
Median Moisture Content (%)	31
Minimum Moisture Content (%)	18
Maximum Moisture Content (%)	90
Number of Samples	75

6.2.4 Mercury Fluxes to Sediments

Because sedimentation rates have been measured at all box-core stations (Edgington and Robbins 1997b, Robbins and Edgington 1997), mercury fluxes were calculated for each site (Table 6-7). The flux is equal to the Pb-210 sedimentation rate times the mercury concentration. At locations where box cores could not be collected, the net sedimentation rate is essentially zero; hence, the net flux is also zero. With a mean of 7.2 ng/cm^2/y, mercury fluxes ranged between 0.85 and 32 ng/cm^2/y (Table 6-8).

Table 6-7. Net Mercury Flux to Lake Michigan Surface Sediments

Station Number*	Total Hg Flux (ng/cm²/y)	Station Number*	Total Hg Flux (ng/cm²/y)
7	6.4	54	0.94
9	19	55	31
9	2.3	58	4.8
13	3.8	61	18
15	23	62	1.1
17	1.4	63	4.0
18	2.2	65	1.6
19	8.4	66	6.2
21	2.9	70	14
21	3.9	78	2.8
22	17	79	5.8
24	10	80	2.8
25	4.5	82	13
26	2.2	83	6.4
27	4.7	85	3.8
29	6.0	86	4.4
31	3.2	87	16
33	2.0	97	3.2
33	3.8	99	5.2
34	5.0	101	7.5
36	8.1	103	3.3

Table 6-7. Net Mercury Flux to Lake Michigan Surface Sediments

Station Number*	Total Hg Flux (ng/cm²/y)	Station Number*	Total Hg Flux (ng/cm²/y)
37	2.7	107	5.4
39	8.5	108	8.0
41	32	110	2.6
46	6.5	112	9.4
48	0.85	120	8.0
53	1.9	126	7.1

* The station numbers used for the sediment sample collection effort do not correspond to the station identifiers used for the open-lake water samples described in Chapter 5.

Table 6-8. Summary Statistics for Net Mercury Fluxes to Lake Michigan Surface Sediments in Depositional Basins

Descriptive Statistic	Result
Mean Net Mercury Flux (ng/cm^2/y)	7.2
Standard Deviation of Mean Net Flux (ng/cm^2/y)	6.9
Median Net Mercury Flux (ng/cm^2/y)	4.9
Minimum Net Mercury Flux (ng/cm^2/y)	0.85
Maximum Net Mercury Flux (ng/cm^2/y)	32
Number of Samples	54

6.2.5 Horizontal Variation of Mercury and Mercury Fluxes

Mercury concentrations and their resulting fluxes varied with location in the lake. Mercury concentrations were higher along the eastern side of the lake than its western side (Figure 6-3). Mercury concentration contours were coincident with those for the bathymetry of the lake (Figure 6-4). Unlike the concentration contours, those for mercury flux were not coincident with the lake bathymetry (Figure 6-5). Regions of highest flux were compressed along the eastern side of the lake.

Figure 6-3. Mercury Concentrations (mg/kg) in Lake Michigan Surficial Sediments (1994-1996)

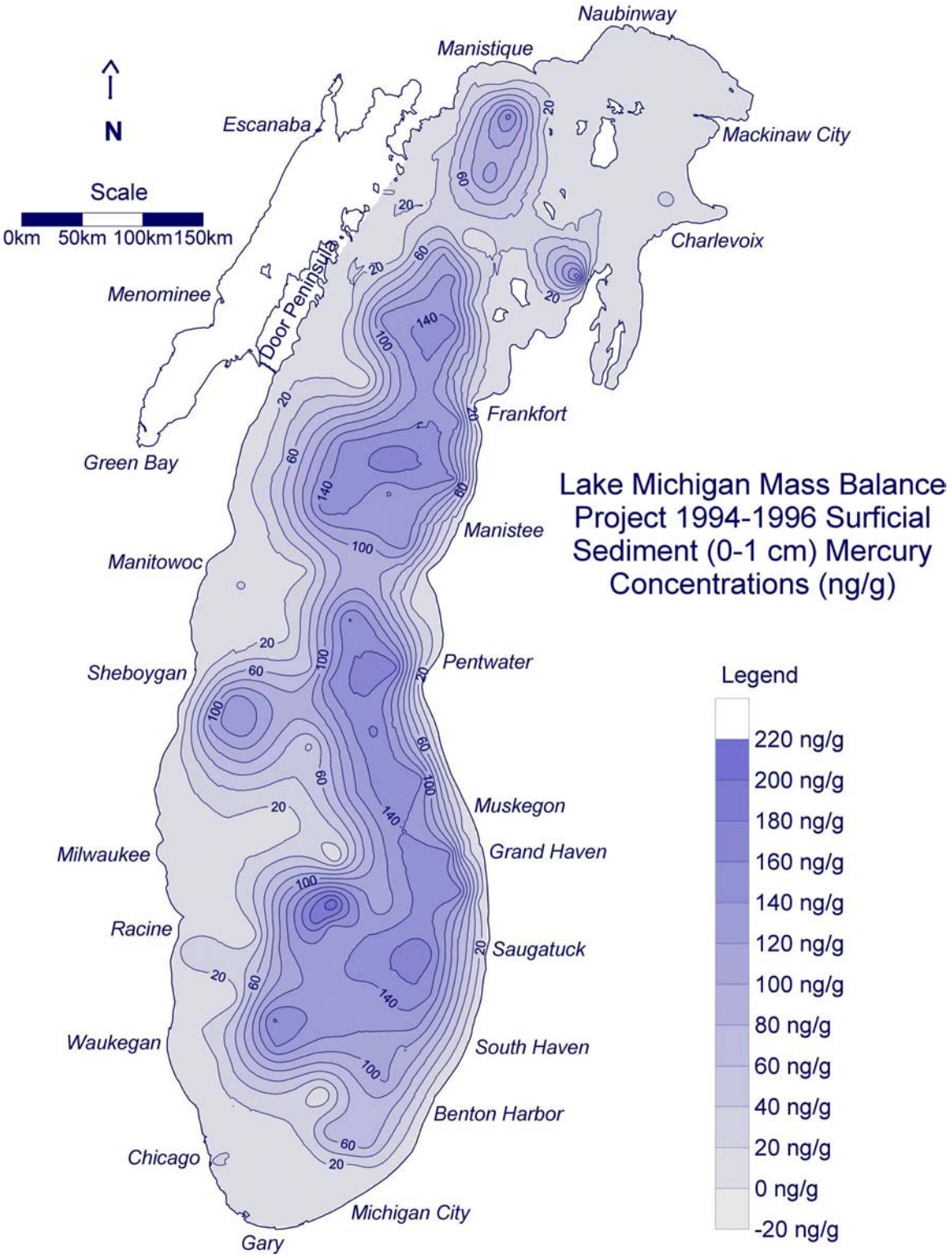


Figure 6-4. Lake Michigan Bathymetry with Depositional Basin Locations

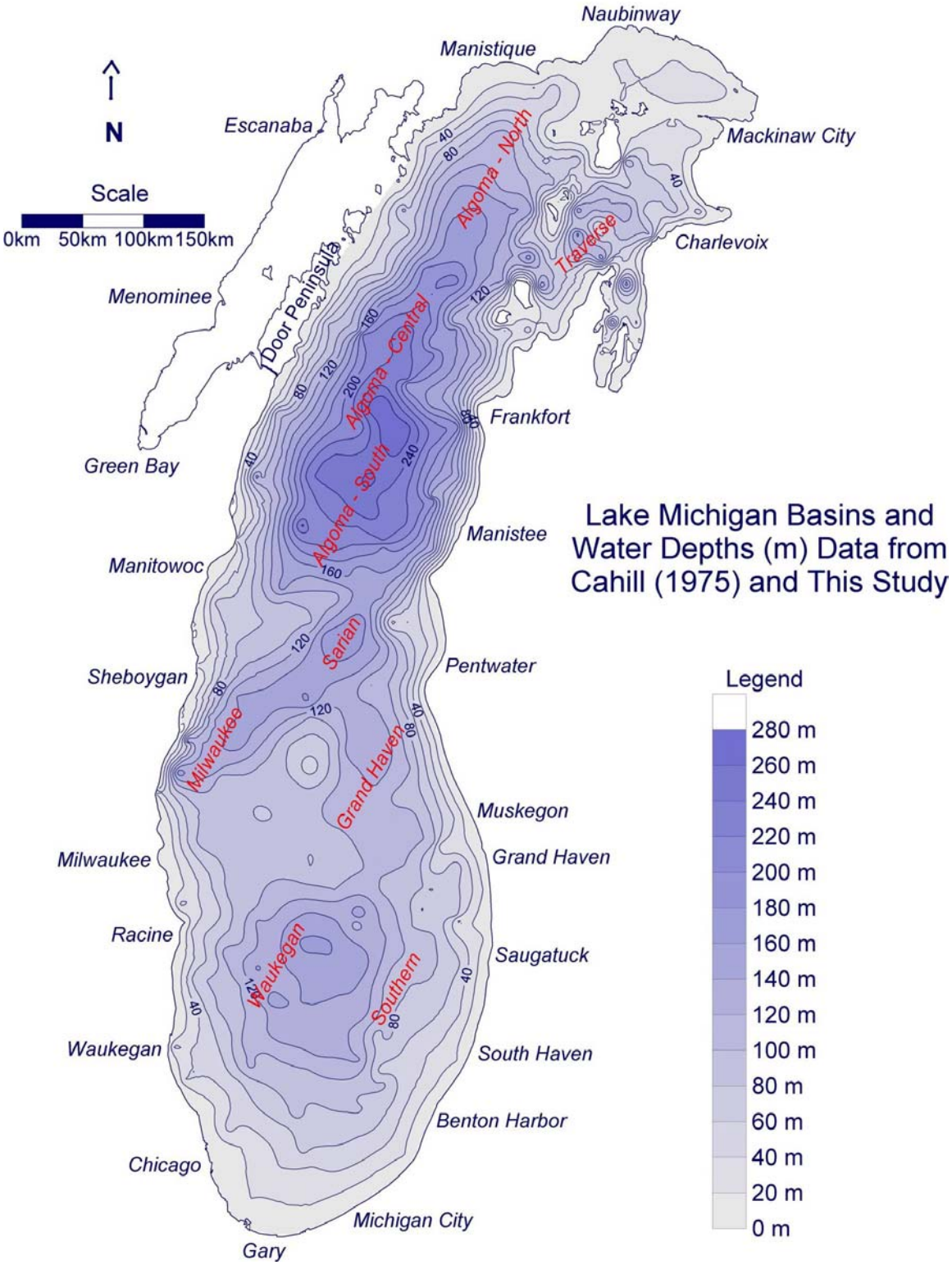
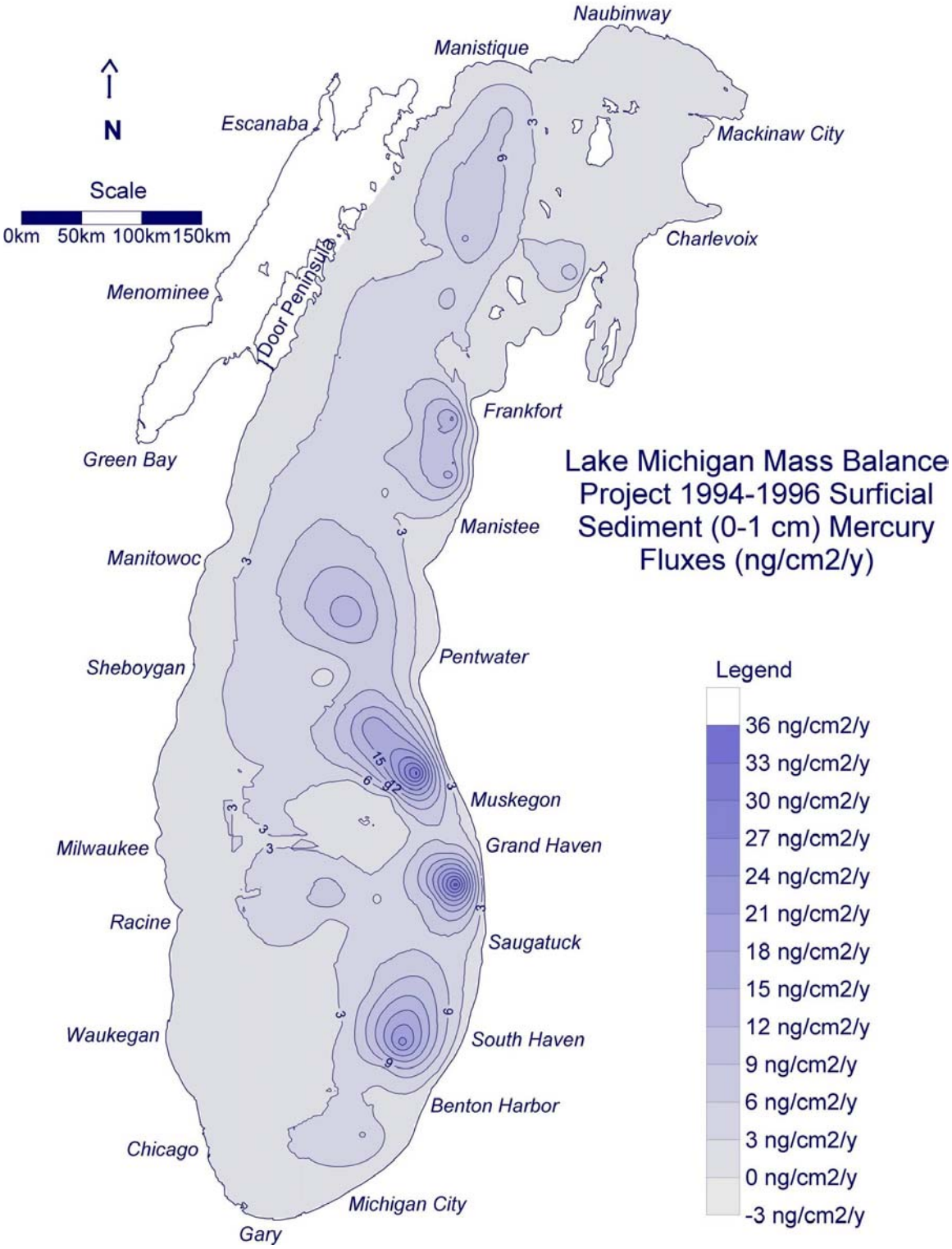


Figure 6-5. Mercury Fluxes (ng/cm²/y) to Lake Michigan Surficial Sediments (1994-1996)



6.3 Quality Assurance

As described in Section 1.5.5, the LMMB quality assurance program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of measurement quality objectives (MQO) for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of data quality issues for the sediment mercury data is provided below.

As discussed in Section 6.1.2, the mass of resuspended sediment collected from the sediment traps was often too small to complete all analyses targeted in the LMMB Study. Because trap samples were collected and analyzed for mercury only during relatively high sediment flux periods, the mercury concentrations measured in sediment traps reflect those in resuspended sediments during these higher flux periods.

For some field and quality control (QC) samples, multiple analyses were conducted either on the field sample or the sample extract. Sample results were reported as average values of replicate results when available and are identified as average values in the Great Lakes Environmental Database (GLENDA) database. A standard reference material (SRM) from the National Institute of Standards and Technology (NIST) was included with sample batches to monitor performance of the analytical system. The Buffalo River Sediment, SRM 2704 (no longer available), has a certified value of 1.47 mg/kg. SRM samples were prepared and analyzed using the same extraction procedure as the field samples and were included with every group of samples extracted. Laboratory reagent blanks also were included with sample batches and were prepared and analyzed using the same extraction procedure as the samples. The mean mercury concentration measured in the blanks in a given batch was used to assess blank contamination in each sample. More than 80% of blanks were below the method detection limit (MDL).

Sediment samples were extracted using two different procedures. Most surficial sediments were extracted using a Leeman Labs, Inc. automated mercury system (Leeman Labs, Inc., 1993). All sediment trap samples and a few surficial sediment samples were extracted using a microwave digestion system (Uscinowicz and Rossmann, 1997). The Leeman automated extraction uses 50% aqua regia and potassium permanganate solutions and is more vigorous than the microwave extraction, which uses a 10% nitric acid solution. Mean recoveries of mercury in the NIST standard reference material samples were 97% for the automated digestion and 90% for the microwave digestion. This may be due, in part, to the smaller sediment sample mass that is used in the microwave digestion procedure compared to the automated digestion procedure, which requires as much as ten times the sample mass used in the microwave procedure. Also, the concentration of acid used in the extraction is greater for the automated extraction. Regardless of the extraction method, mercury concentrations measured in the SRM samples were within acceptance criteria for 100% of the sample analyses.

As discussed in Section 2.6, all data were verified by comparing the field and QC sample results produced by each principal investigator (PI) with their MQOs and with overall LMMB Study objectives. Field sample results were flagged when pertinent QC sample results did not meet acceptance criteria defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 6-9 provides a summary of flags applied to the sediment mercury data. The summary provided below includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6.

Table 6-9. Summary of Data Verification Flags Applied to Routine Field Sample Results for Sediment Mercury

Flag	Number of QC Samples	Percentage of Samples Flagged
EHT, Exceeded Holding Time	—	0
FBS, Failed Blank Sample	41 lab reagent blank samples	0
FDL, Failed Lab Duplicate	34 lab duplicate pairs	2% (4)
FFD, Failed Field Duplicate	4 field duplicate pairs	1% (2)
FSR, Failed Standard Reference Material	40 SRM samples	0
GTL, Greater than Operating Range	—	3% (5)
SCX, Suspected Contamination	—	2% (3)
UDL, Below Sample Specific Detection Limit	—	<1% (1)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

All of the sediment samples were analyzed for mercury within the required holding time. Of the 41 laboratory reagent blank samples (LRBs) prepared and analyzed, none of the sample results exceeded the MQO and therefore, none of the routine field samples were flagged for a failed blank sample (FBS). Only 2% of the field sample results had associated laboratory duplicates with results above the maximum RPD/RSD of 15%, the acceptance criteria. The maximum RPD/RSD for these sample groups was 48%. Three percent of samples contained mercury concentrations that were greater than the operating range of the analytical system. These results are flagged in the database and should be considered estimated values. Two percent of the field samples were flagged for suspected contamination, based on laboratory notation that the samples were potentially contaminated during sample preparation and analysis in the laboratory. The laboratory notation is included in the database for these sample results in a comment field (exception to method text).

MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on three of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 6-10 provides a summary of data quality assessments for several of these attributes for the sediment mercury study data.

Table 6-10. Data Quality Assessment for Mercury in Sediment Samples

Parameter	Number of QC Samples	Assessment
Number of Routine Samples Analyzed	—	191
System Precision Mean Field Duplicate RPD (%), Samples >MDL_S	4 field duplicate pairs	38%
Analytical Precision Mean Lab Duplicate RPD (%), Samples >MDL_S	30 lab duplicate pairs	8.5%
Analytical Bias, Mean SRM[3] (%)	40 SRM samples	92%
Analytical Sensitivity, Samples reported as <MDL_S (%)	—	0.5%

MDLs = Sample Specific Detection Limit
SRM = Standard Reference Material, Buffalo River Sediment, SRM 2704 (NIST 1990)

System precision, estimated as the mean relative percent difference for field duplicates, was 38%. However, because only four field duplicates were collected and analyzed, this estimate may not accurately reflect the variability associated with sampling and analytical activities. Analytical precision, estimated as the mean relative percent deviation for laboratory duplicates, was much lower, at 8.5%, suggesting that either the small number of field duplicates did not accurately reflect the variability associated with sampling and analytical activities, or the variability associated with sampling is much greater than that associated with the analytical activities. This latter possibility is not unexpected for sediment sampling. Analytical bias, estimated as the mean recovery of standard reference materials, was 92%, which indicates a slight low bias in the analytical results. More than 99% of samples contained mercury concentrations above the detection limit.

6.4 Data Interpretation

Lake Michigan surficial sediments have elevated mercury concentrations compared to pre-settlement concentrations. Fluxes of mercury to the lake from atmospheric, tributary, and shoreline sources are redistributed within the lake by wave action and current transport. This leads to a definitive distribution pattern of mercury concentrations in Lake Michigan sediments and fluxes to those sediments. Only the mercury results for surficial sediment are discussed in this chapter. A discussion of moisture content is not included in this chapter.

6.4.1 Comparison to Other Great Lakes Sediments

Excluding Green Bay, Lake Michigan surficial sediments have relatively low mercury concentrations (Table 6-11).

Table 6-11. Comparison of Lake Michigan Surficial Sediment Mercury Concentrations to those at other Locations in the Great Lakes Basin

Location and Years	N	Mean (ng/g)	Standard Deviation (ng/g)	Median (ng/g)	Minimum (ng/g)	Maximum (ng/g)	Reference and Surficial Interval Sampled
Green Bay 1987 - 1990	74	360	270	280	6	1100	Rossmann and Edgington (2000) 0-1 cm
Superior 1983	31	180	180	140	27	960	Rossmann (1999) 0-2 cm
North Channel 1973	55	150	230	NA	8	1100	Thomas (1974) 0-3 cm
Georgian Bay 1973	117	260	1000	NA	12	9500	Thomas (1974) 0-3 cm
Huron 1969	163	220	160	NA	54	800	Thomas (1974) 0-3 cm
St. Clair 1970	55	630	630	NA	70	2600	Thomas (1974) 0-3 cm
Erie 1971	243	610	700	NA	13	7500	Thomas (1974) 0-3 cm
Ontario 1968	248	650	510	NA	32	2100	Thomas (1974) 0-3 cm
Michigan 1994 - 1996	118	78	65	73	2	260	Rossmann (this study) 0-1 cm

NA = Not applicable

In the main basin of Lake Michigan, mean mercury concentration is nearly one-half of those found in all the other Great Lakes, making the lake relatively uncontaminated with mercury. However, it should be noted that Lake Michigan sediments are being compared to much earlier results for other locations. Contamination of sediments was historically higher than at present. It should also be noted that the surficial sediment intervals compared are different in thickness and represent different periods of time that are integrated to produce the mercury concentration reported for the homogenized layer of sediment. Due to the difference in sampling year and sediment thickness, cautions should be used when comparing LMMB data to these other studies. Recent data having similar time intervals represented by the top interval are insufficient to be representative of Lakes Superior, Huron, Erie, and St. Clair sediments.

Note should be made of the fact that Green Bay, a bay of Lake Michigan, has sediments that are contaminated with mercury relative to other Great Lakes locations. The contamination of these sediments has been attributed to historical industrial practices in the Fox River drainage basin (Rossmann and Edgington, 2000).

6.4.2 Comparison to Historical Lake Michigan Concentrations

For Lake Michigan, several historic data sets exist for mercury in surficial sediments (Table 6-12). Kennedy *et al.* (1971) reported on mercury concentrations in the 0-1 and 0-5 cm intervals of surficial sediments collected during 1969 and perhaps 1970. Samples were collected from the southern basin of Lake Michigan from 31 sites (Figure 6-6). A much more comprehensive collection was made in 1975 and reported in Cahill (1981). The surficial 3 cm of sediment were collected from 254 locations from all basins of the lake (Figure 6-7). Mercury results are available for one of three sediment cores collected from southern Lake Michigan in 1981 (Figure 6-8). Results for the LM-81-HS core are reported by Pirrone *et al.* (1998). Additional details for that core are reported here.

Table 6-12. Comparison of Current Lake Michigan Results to Historical Data

Years Collected	N	Mean (ng/g)	Standard Deviation (ng/g)	Median (ng/g)	Minimum (ng/g)	Maximum (ng/g)	Reference and Surficial Interval Sampled
1969-1970?	31	150	100	120	30	380	Kennedy *et al.* (1971) surficial 0-1 through 0-5 cm
1975	254	110	110	60	20	670	Cahill (1981) 0-3 cm
1981	1	200	—	—	—	—	Pirrone *et al.* (1998) 0.5 cm
1994-1996	118	78	65	73	2	260	Rossmann (this study) 0-1 cm

Figure 6-6. Station Locations for the 1969-1970 Kennedy *et al*. Mercury Results

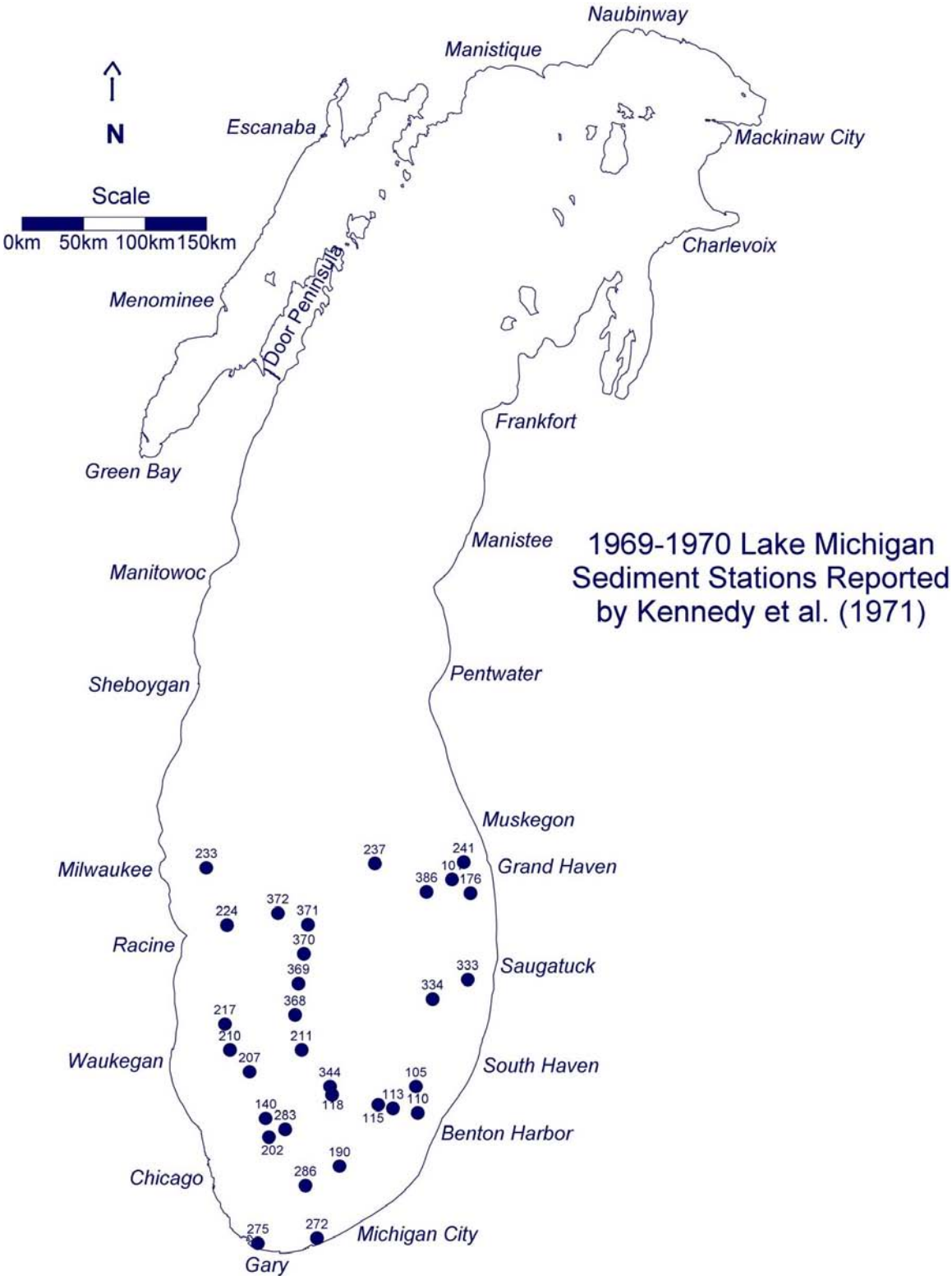


Figure 6-7. Station Locations for the 1975 Cahill Mercury Results

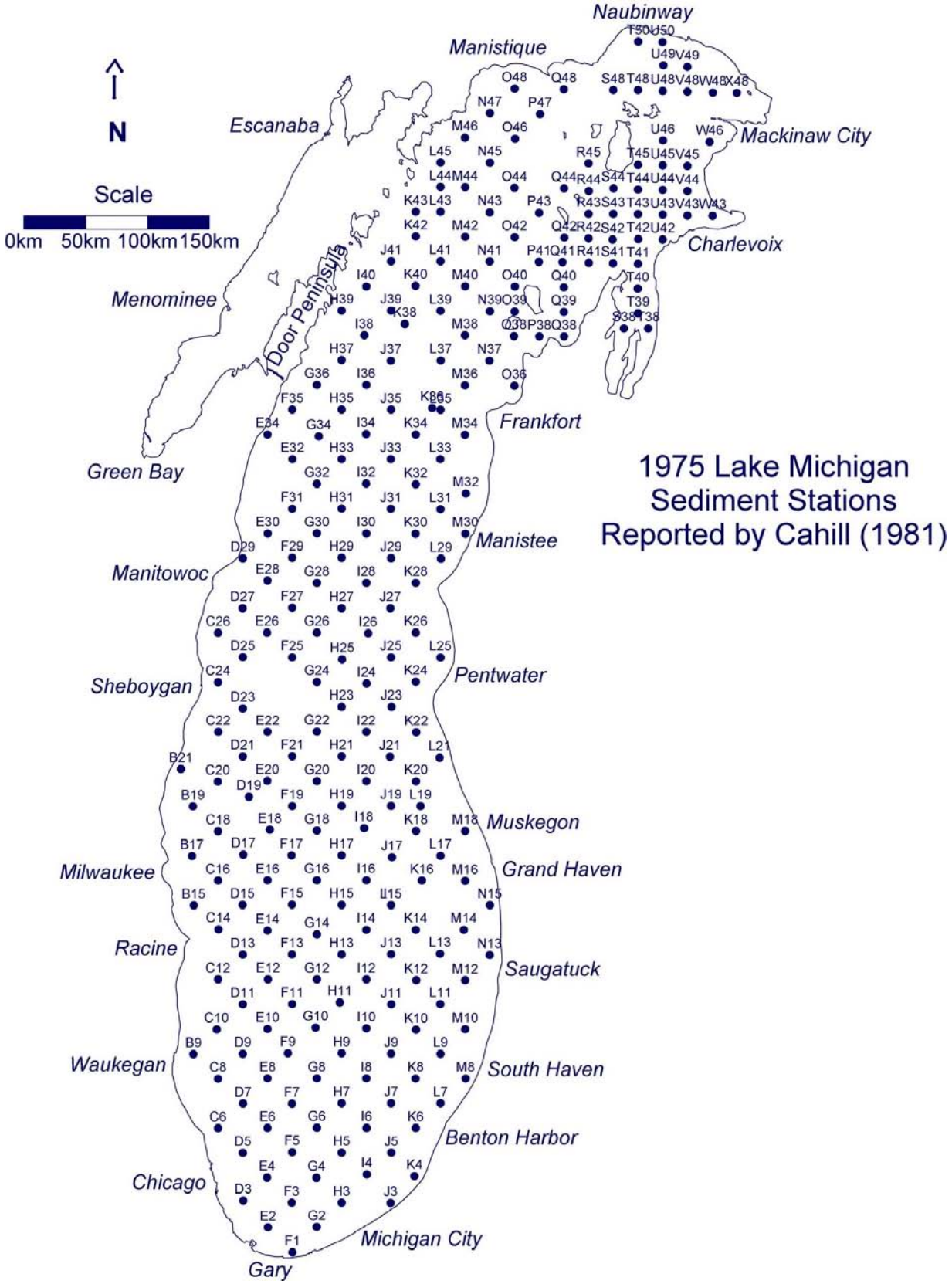
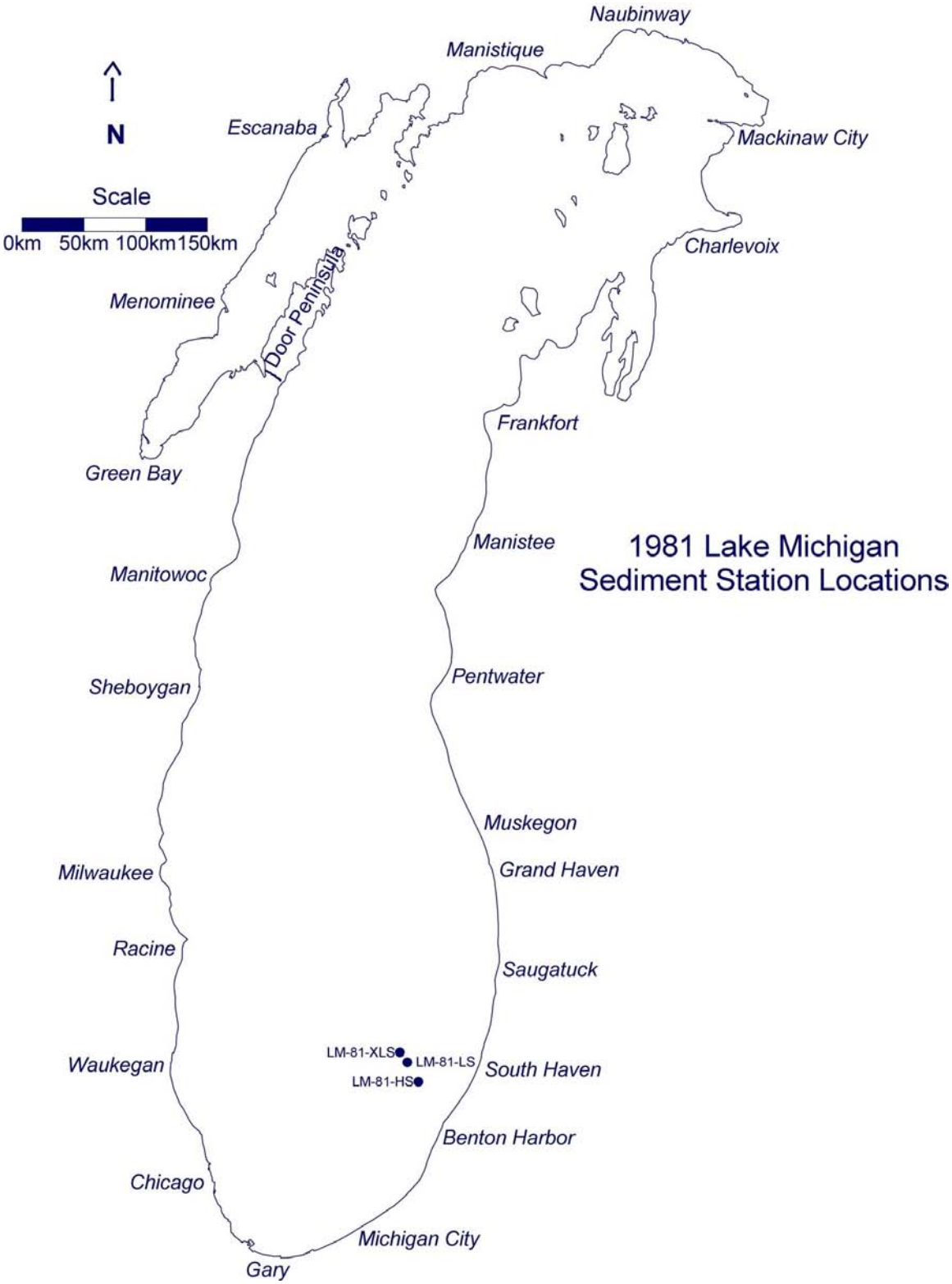


Figure 6-8. Station Locations for 1981 Sediment Cores



A general comparison of these results can be potentially misleading. It appears that mercury may be decreasing in surficial sediments between 1969 and 1996. The problem is derived from using grab samples that penetrated a variety of sediment depths and sampled a variety of sediment types. Samples reported by Cahill (1981) represented a homogenate of the surficial 3 cm. It is possible that collection to a depth of 3 cm penetrated to older sediments generally known to be more contaminated with mercury, skewing the results toward a higher concentration (Rossmann and Edgington, 2000). Also, samples collected in 1975 and 1994-1996 were representative of a variety of sediment types. Samples collected from sandy areas will skew the results toward lower mercury concentrations. Mercury is associated with fine-grained sediments. Depending upon the station distribution for a data set, results may be biased to various regions of the lake basin. Thus, a direct comparison of data set that have different station distributions and different depths of surficial sediment can lead to incorrect conclusions. To avoid these problems, it is best to compare only those sediments collected at the same sampling interval from the same station in a depositional basin.

There is only one location for which a direct comparison with historical data may be made. LMMB Station 15 (Figure 6-1) is coincident with Station K8 reported by Cahill (1975). It is within 5 km of Station 105 reported by Kennedy *et al*. (1971) and Station LM-81-HS reported by Pirrone *et al*. (1998). Two comparisons can be made. The first is a comparison for the surficial sample interval of 0 - 3 cm sediment depth, and the second is a comparison for the interval of 0 - 1 cm sediment depth. For the 0 - 3 cm surficial sediment depth interval, there is a distinct decrease in mercury concentration between 1969 and 1975 which continues through 1981 (Table 6-13).

Table 6-13. Comparison of Lake Michigan Results at Station 15 to Historical Results for the 0 - 3 cm Surficial Sediment Interval

Year Collected	Mercury Concentration (ng/g)	Reference and Surficial Interval Sampled
1969	300	Kennedy *et al*. (1971)
1975	240	Cahill (1975)
1981	180	Pirrone *et al*. (1998)

This decrease is also evident for the 0 - 1 cm surficial sediment depth interval comparison (Table 6-14). Thus, there has been a decrease in mercury concentrations in surficial sediments between 1969 and 1994. The decrease between 1969 and 1975 was at the rate of 4.3 ng/cm^2/y and that between 1975 and 1981 was 10 ng/cm^2/y. The resolution for these 0 - 3 cm of surficial sediments was roughly 5 years. A more realistic recent rate of mercury decline is derived from the 0 - 1 cm results, where the resolution is less than one year. The most recent rate of decrease between 1981 and 1994 was 3.8 ng/cm^2/y.

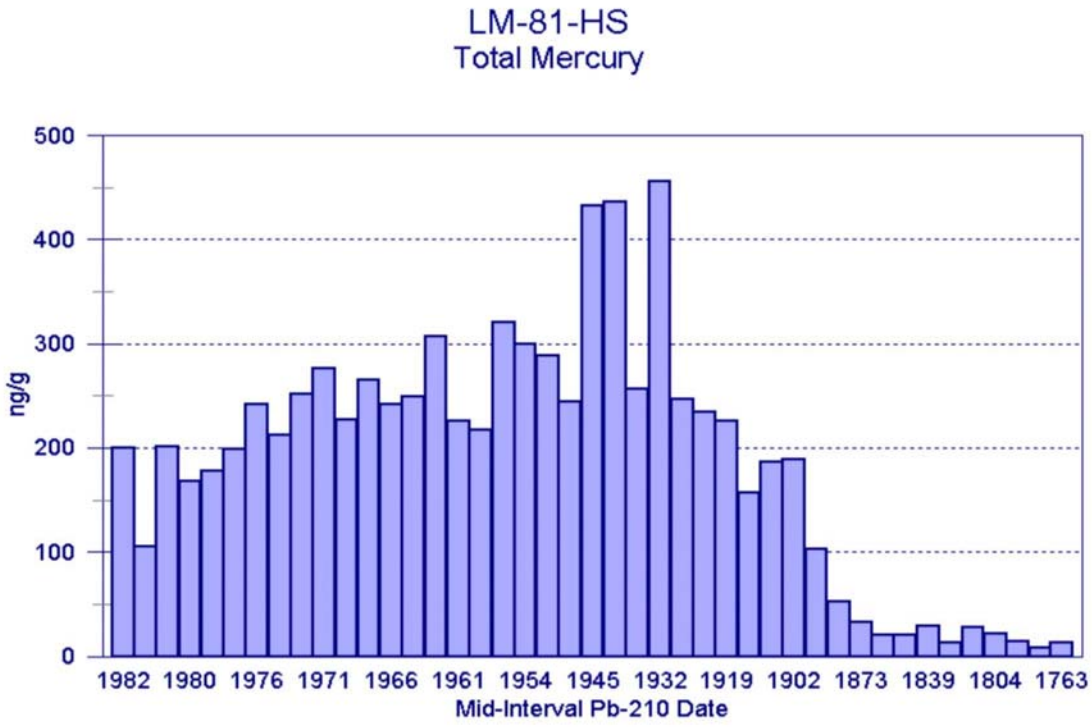
Table 6-14. Comparison of Lake Michigan Results at Station 15 to Historical Results for the 0 - 1 cm Surficial Sediment Interval

Year Collected	Mercury Concentration (ng/g)	Reference and Surficial Interval Sampled
1981	150	Pirrone *et al*. (1998)
1994	100	This study

The recent decrease in mercury concentrations in surficial sediments is corroborated by results for the 1981 core that are reported by Pirrone *et al*. (1998) and presented in a slightly different manner here (Figure 6-9). At this station, pre-1800 background mercury concentrations ranged between 8 and 14 ng/g. Between 1930 and 1950, peak mercury concentrations as high as 460 ng/g were reached. By the late 1950s, mercury reached its maximum concentration ranging between 300 and 450 ng/g. After 1970,

mercury concentrations began to decrease. The decrease that was noted in the 1981 core has continued through 1994 at this location in the lake.

Figure 6-9. Vertical Variation of Mercury in Core LM-81-HS



Each bar represents one interval of the core.

6.4.3 Comparison to Historical Lake Michigan Horizontal Variations

Horizontal variations of mercury in surficial sediments can be compared to two previously published data sets. As discussed in the previous section, absolute concentrations cannot be compared; however, patterns of variation can be discussed. The Kennedy *et al*. (1971) data set for the period of 1969-1970 covers southern Lake Michigan (Figure 6-6). The distribution pattern (Figure 6-10) is similar to that for 1994-1996 (Figure 6-3) and mimics the bottom topography (Figure 6-4). The same is true for the Cahill (1981) data set collected in 1975 (Figure 6-11). The 1975 data set is very extensive and includes stations from the entire lake (Figure 6-7). These two data sets and the current one produce mercury distribution patterns that are similar and conform to the lake's bathymetry, sediment and mercury sources, and water circulation pattern.

Figure 6-10. Mercury Concentrations (mg/kg) in 1969-1970 Lake Michigan Surficial Sediments

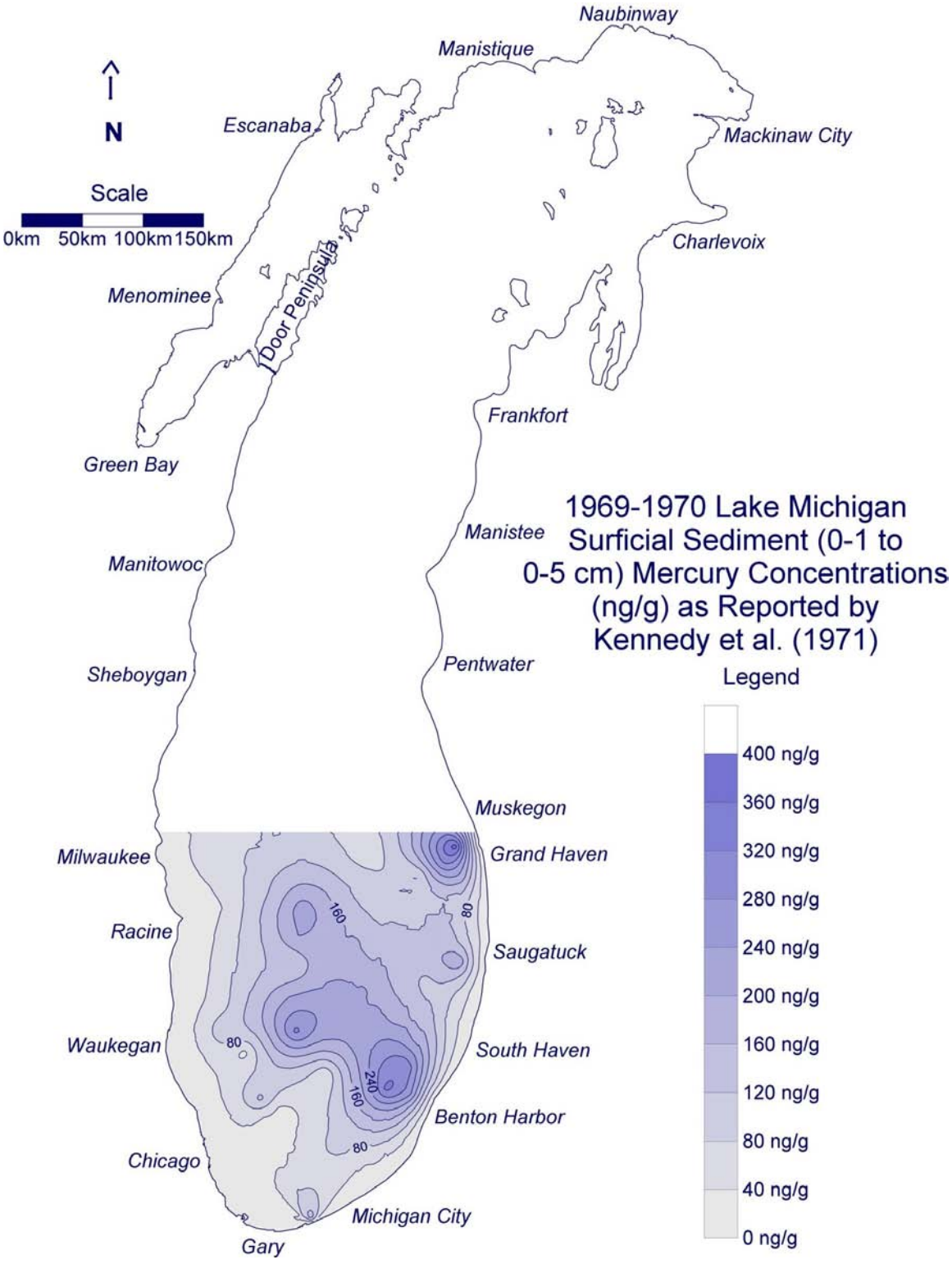
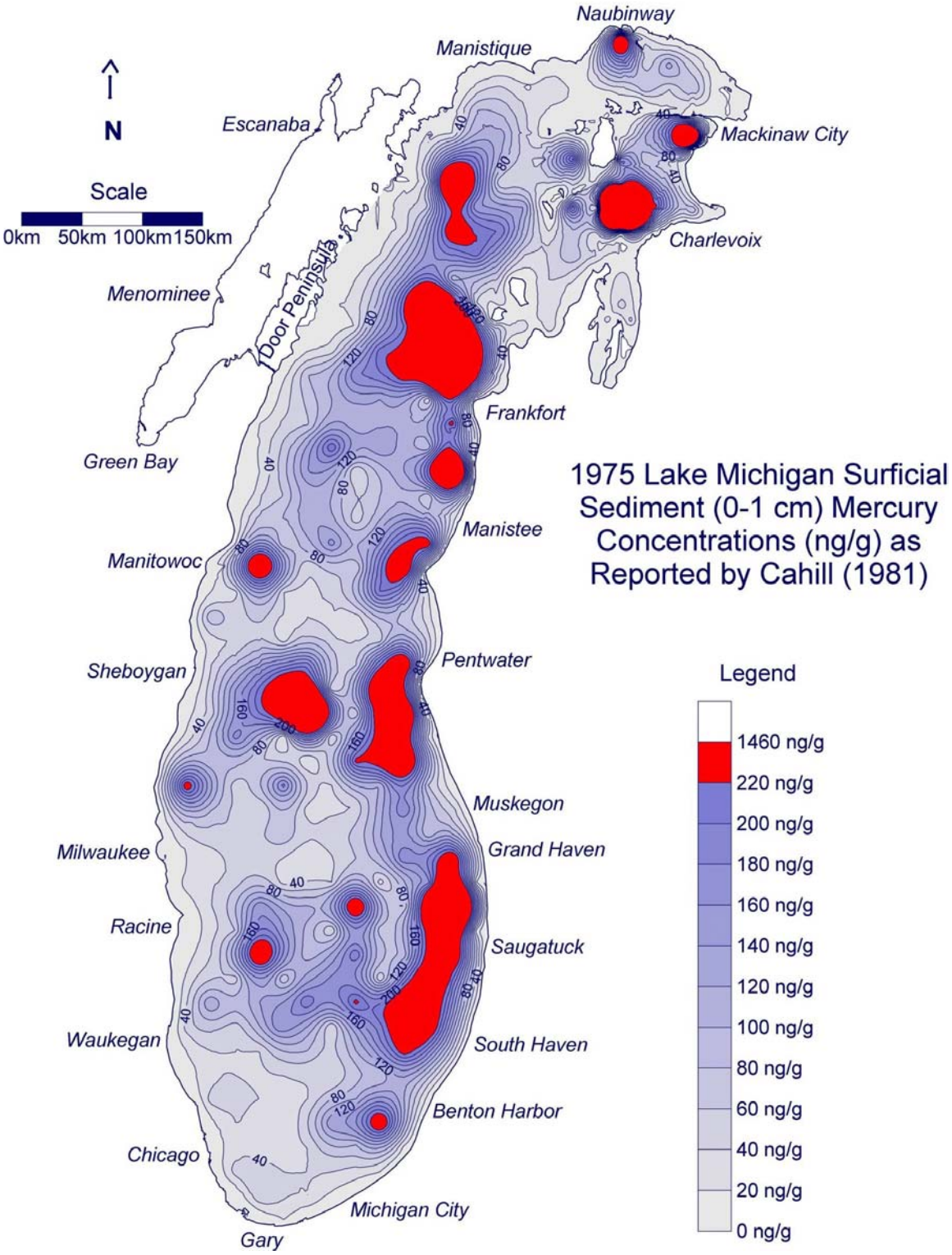


Figure 6-11. Mercury Concentrations (mg/kg) in 1975 Lake Michigan Surficial Sediments



6.4.4 Regional Lake Michigan Comparisons

Because bathymetry and currents control observed mercury distributions in surficial sediments, it is important to compare regional mercury concentrations for only the depositional basins of the lake (Table 6-15). When this is done, it becomes apparent that the mean mercury concentration varies very little between basins. Mean mercury concentrations range between 120 and 160 ng/g, within the observed standard deviations (Table 6-15). Two anomalies are noteworthy. First, the minimum concentration in the Southern Basin is substantially lower than those for the other basins. The reason for this is unknown. Second, the maximum concentration for the Waukegan Basin is considerably higher than those for the other basins, suggesting a historic or current source, containing high mercury concentrations, to that basin. Other than these noted differences, the sediments in the lake's depositional basins are amazingly similar, suggesting either a similar regional source of mercury to the lake most likely delivered through atmospheric pathways, or a well-mixed lake that redistributes inputs extremely well prior to sedimentation to the lake bottom.

Table 6-15. Comparison of Mercury Concentrations in Various Basins of Lake Michigan for Box Cores Only

Basin	N	Mean (ng/g)	Standard Deviation (ng/g)	Median (ng/g)	Minimum (ng/g)	Maximum (ng/g)
Southern	15	120	31	130	72	180
Waukegan	11	160	65	130	100	320
Grand Haven	6	150	19	150	120	170
Milwaukee	3	130	15	130	110	140
Sarian	1	160	—	—	—	—
Algoma South	8	140	17	140	120	180
Algoma Central	7	130	15	130	100	150
Algoma North	2	130	—	—	110	150
Traverse	1	160	—	—	—	—

6.4.5 Mercury Fluxes

The amount of material available in trap samples limited the number of samples available for mercury analyses. This limitation translates to a data bias because trap samples having enough material available for mercury analysis represent relatively high sediment flux periods. As a result, mercury fluxes to traps (0.049 to 3.7 ng/cm^2/d) are always higher than fluxes to the sediment (0.0055 to 0.063 ng/cm^2/d) at the trap locations. Therefore, further discussion of mercury concentrations in and fluxes to sediment traps is not warranted due to the bias.

As with mercury concentrations, mean mercury fluxes did not significantly vary from basin to basin of the lake (Table 6-16). All fluxes were within one standard deviation of one another. Of interest are the considerably higher minimum fluxes to the Algoma Basin relative to the other basins. In general, basins that are towards the west side of the lake have lower mean and median fluxes than those on the east side of the lake. Of significant note are the relatively high maximum mercury fluxes to the Southern and Grand Haven Basins. Both of these basins are on the east side of the lake. These high fluxes could be related to the transport of materials from the southwestern and southern shore of the lake to the eastern shore, especially in the spring. This event occurs annually and the resulting plume has suspended particulate matter concentrations 4 to 10 times that of the lake (Eadie *et al*., 1996). A large amount of particulate matter, with its associated contaminants, is transported along the eastern shore, where it settles to the lake floor and accumulates in the Southern and Grand Haven deposition basins (Figure 6-5).

Table 6-16. Comparison of Total Mercury Fluxes to Various Basins of Lake Michigan for Box Cores Only

Basin	N	Mean (ng/cm²/y)	Standard Deviation (ng/cm²/y)	Median (ng/cm²/y)	Minimum (ng/cm²/y)	Maximum (ng/cm²/y)
Southern	15	10	8.7	6.5	0.85	32
Waukegan	11	3.4	1.9	2.9	1.4	8.5
Grand Haven	6	10	12	4.0	0.94	31
Milwaukee	3	3.3	1.9	4.0	1.1	4.8
Sarian	1	14	—	—	—	—
Algoma South	8	6.9	4.9	5.1	2.8	16
Algoma Central	7	5.2	2.5	5.2	2.6	9.5
Algoma North	2	7.6	—	—	7.1	8.0
Traverse	1	8.0	—	—	—	—

Fluxes to Lake Michigan in the vicinity of Station 15 (Figure 6-1) have decreased since 1981. In order to compare fluxes between the two years, it is necessary to correct fluxes for sediment focusing. Sediment focusing is the process by which fine-grained particles and their associated contaminants are winnowed from the coarser fraction of sediments by wave and current action. Winnowing and resuspension occurs in regions that are shallow enough to have wave and current velocities high enough to initiate sediment grain movement. The resuspended materials are transported until they settle from the water column. For each particle and associated contaminants, the process is repeated until the particle settles in a region where winnowing and resuspension no longer occur. These regions are the depositional basins. For the contaminants that are preferentially associated with fine-grained sediment particles, the resuspension/transport process can result in a depletion or enhancement of a contaminant's net flux to any one location. For sedimentary basins, the result is an enhancement of contaminate concentrations and fluxes called sediment focusing. Sediment focusing can be estimated using parameters whose fluxes to a lake's surface are equal at all locations. This is true for historically bomb-generated Cs-137 whose fluxes to the region are well documented, and naturally derived Pb-210, whose flux is well known. Both of these are mixed well in the atmosphere and were deposited to the lake's basin as a uniform flux from the atmosphere. Because they, like contaminants, are associated with the fine-grained components of sediment, they also are subject to sediment focusing. Because their fluxes are known, the degree of sediment focusing can be calculated for them and then applied to observed contaminant fluxes. When there is an excess of either of these radionuclides, the focusing factor is greater than one (depositional basins). In regions of active winnowing and resuspension, the focusing factor may be less than one, indicating depletion.

The Pb-210 and Cs-137 focusing factors are not always equal. The reason for this is unknown, but it is reasoned to be related to each radionuclide associating with a different particle type. Because we do not always know which focusing factor to apply to a particular contaminant, an average of the two focusing factors can be used. For this study, however, the Cs-137 focusing factor will be used for the purpose of comparison of Lake Michigan mercury fluxes to those of Green Bay and Lake Superior. For both those locations, the Cs-137 focusing factor was used because only the Cs-137 factor was available for Lake Superior. Mercury fluxes to Lake Michigan are very similar to those for the open waters of Lake Superior, but are considerably lower than those to Green Bay (Table 6-17).

Table 6-17. Comparison of Total Mercury Fluxes for Lake Michigan Corrected for Cs-137 Focusing Factors to Fluxes for other Locations

Location	Mean (ng/cm²/y)	Standard Deviation (ng/cm²/y)	Median (ng/cm²/y)	Reference
Lake Michigan	3.4	1.8	3.2	this study
Lake Superior	3.2	1.1	2.8	Rossmann (1999)
Green Bay	19	30	14	Rossmann and Edgington (2000)

A good illustration of the use of a sediment focusing factor is the region of the lake around Station 15. Total uncorrected mercury fluxes to the surficial 1 cm of sediment are very similar in magnitude (Table 6-18). When corrected for sediment focusing, it becomes apparent that the flux of mercury to this region of the lake has decreased from 13 ng/cm^2/y in surficial sediments collected in 1981, to 4.1 ng/cm^2/y for surficial sediments collected in 1994. This is consistent with the observed trend of decreasing mercury concentrations in surficial sediments.

Table 6-18. Comparison of Mercury Fluxes to Lake Michigan Surficial Sediments at Station 15 in 1981 and 1994

Year	Total Mercury Flux (ng/cm²/y)	Total Mercury Flux Corrected for Focusing Factor (ng/cm²/y)
1981	22	13
1994	23	4.1

6.4.6 Relative Importance of Regional Atmospheric Sources and Point Sources of Mercury

To estimate the relative contribution of regional atmospheric and local point-source mercury fluxes to measured total mercury fluxes, the total mercury fluxes were corrected with the Cs-137 focusing factor. For Lake Michigan, atmospheric mercury fluxes account for 50% of the total mercury flux. This is higher than that for Lake Superior (38%) and Green Bay (15%). Fluxes of mercury to Green Bay are dominated by point sources derived from historic industrial use of mercury within the region (Rossmann and Edgington, 2000).

6.5 Conclusions

Lake Michigan surficial sediments have low mercury concentrations relative to Green Bay. The mean concentration was 0.078 mg/kg. The mean net total mercury flux to the depositional basins was 7.2 ng/cm^2/y. Mercury fluxes to Lake Michigan sediments were similar to those for Lake Superior open-water sediments and considerably lower than those to Green Bay sediments. There was little variation in mercury concentration or fluxes from basin to basin of the lake. Mercury concentration distribution patterns in surficial sediments are similar to historic patterns and conform to the bathymetry. Fluxes do not conform to the bathymetry and are elevated along the eastern shore of the lake. Regional atmospheric fluxes of mercury account for 50% of the total mercury flux to recent surficial sediments. Both mercury concentrations in, and fluxes to, surficial sediments have decreased since the 1970s.

Chapter 7
Mercury in Plankton

7.1 Results

Phytoplankton and zooplankton were collected in Lake Michigan from June 1994 through October 1995 for total mercury analysis. Phytoplankton samples were collected by pumping water from the optimum depth in the water column for maximum phytoplankton density through 10-µm phytovibe nets. Zooplankton samples were collected in vertical tows using nested 102-µm and 500-µm plankton nets (see Section 2.4.5 for details of the sample collection procedures). Plankton samples were collected from 15 locations, including 9 stations within 4 designated biological sampling areas (biota boxes) and 6 additional routine monitoring stations (see Figure 2-7 in Chapter 2). A total of 157 samples were collected and analyzed for total mercury by cold vapor atomic fluorescence spectroscopy (Table 7-1).

7.1.1 Variation Among Sample Types

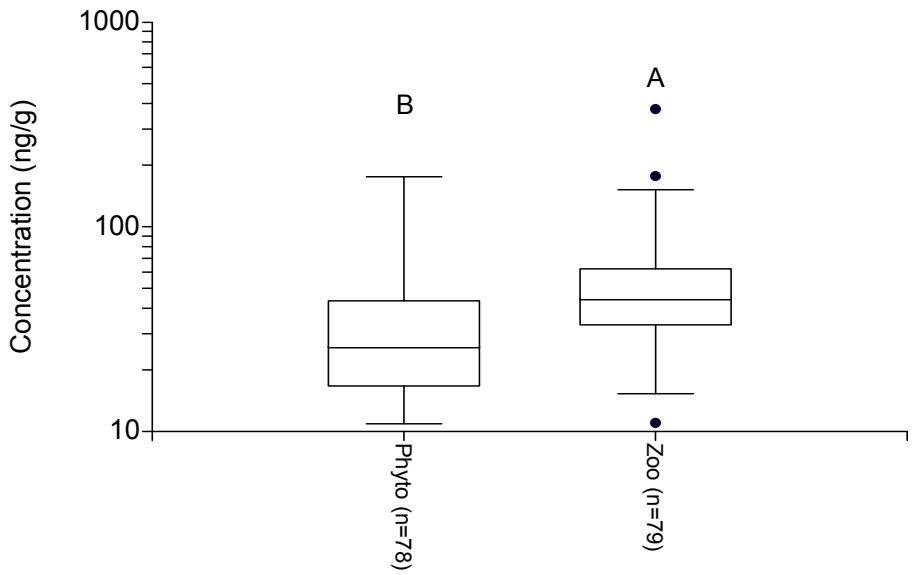
All plankton samples collected from Lake Michigan, except one zooplankton sample, contained total mercury levels above sample-specific detection limits, which averaged 8.65 ng/g for phytoplankton and 7.82 ng/g for zooplankton. Total mercury concentrations in phytoplankton ranged from 10.9 to 176 ng/g and averaged 35.0 ng/g. Total mercury concentrations in zooplankton ranged from 11.0 to 376 ng/g and averaged 54.3 ng/g. Based on a paired *t*-test using log-transformed mercury data, Lake Michigan zooplankton contained significantly higher (at the 95% confidence level) levels of mercury than phytoplankton (Figure 7-1).

The significantly higher levels of mercury found in zooplankton compared to phytoplankton suggest the bioaccumulation and biomagnification of mercury in the lower pelagic food web of Lake Michigan. PCBs and *trans*-nonachlor also were found to bioaccumulate and biomagnify in the Lake Michigan food web (USEPA, 2004). For PCBs and *trans*-nonachlor, a portion of the difference between zooplankton and phytoplankton concentrations was due to the lipid content in the two groups. This was not true for mercury accumulation. Mercury concentrations in zooplankton and phytoplankton were not correlated with lipid content (r^2 of 5% and 0.9% for phytoplankton and zooplankton, respectively), and generalized linear model results showed that lipid content did not explain a significant portion of variability in mercury data either directly, or through interaction with trophic level (phytoplankton/zooplankton). While organic contaminants such as PCBs and *trans*-nonachlor are preferentially accumulated in fatty tissues, mercury does not appear to be preferentially accumulated in such tissues. Mercury has been shown to preferentially bind to sulfhydryl groups in proteins, and in fish, accumulate in muscle tissue (USEPA, 1999b).

Table 7-1. Number of Plankton Samples Analyzed for Mercury in the LMMB Study

Sample Type	Sampling Location		Sampling Dates	Number of Samples Analyzed
	Biota Box	Station		
Phytoplankton	Chicago biota box	05	06/26/94 to 10/10/95	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	6
		140	06/18/94 to 09/23/95	6
		180	06/18/94 to 09/22/95	6
	Port Washington biota box	240	06/21/94 to 10/02/95	5
		280	06/20/94 to 10/01/95	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6
		340	06/25/94 to 10/06/95	6
		380	06/24/94 to 10/06/95	7
	Other	18M	06/22/94 to 10/08/95	6
		23M	06/23/94 to 10/03/95	6
		27M	06/20/94 to 08/10/95	3
		40M	08/12/94 to 04/12/95	3
		47M	06/17/94 to 09/19/95	5
	Total			78
Zooplankton	Chicago biota box	05	06/26/94 to 10/10/95	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	6
		140	06/18/94 to 09/23/95	6
		180	06/18/94 to 09/22/95	5
	Port Washington biota box	240	06/21/94 to 10/02/95	6
		280	06/20/94 to 10/01/95	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6
		340	06/25/94 to 10/06/95	6
		380	06/24/94 to 10/06/95	7
	Other	18M	06/22/94 to 10/08/95	6
		23M	08/19/94 to 10/03/95	5
		27M	06/20/94 to 08/10/95	4
		40M	10/18/94 to 04/12/95	2
		47M	06/17/94 to 09/19/95	6
		19M	01/24/95 to 01/24/95	1
	Total			79
Total				157

Figure 7-1. Mercury Concentrations in Phytoplankton and Zooplankton Measured in Lake Michigan



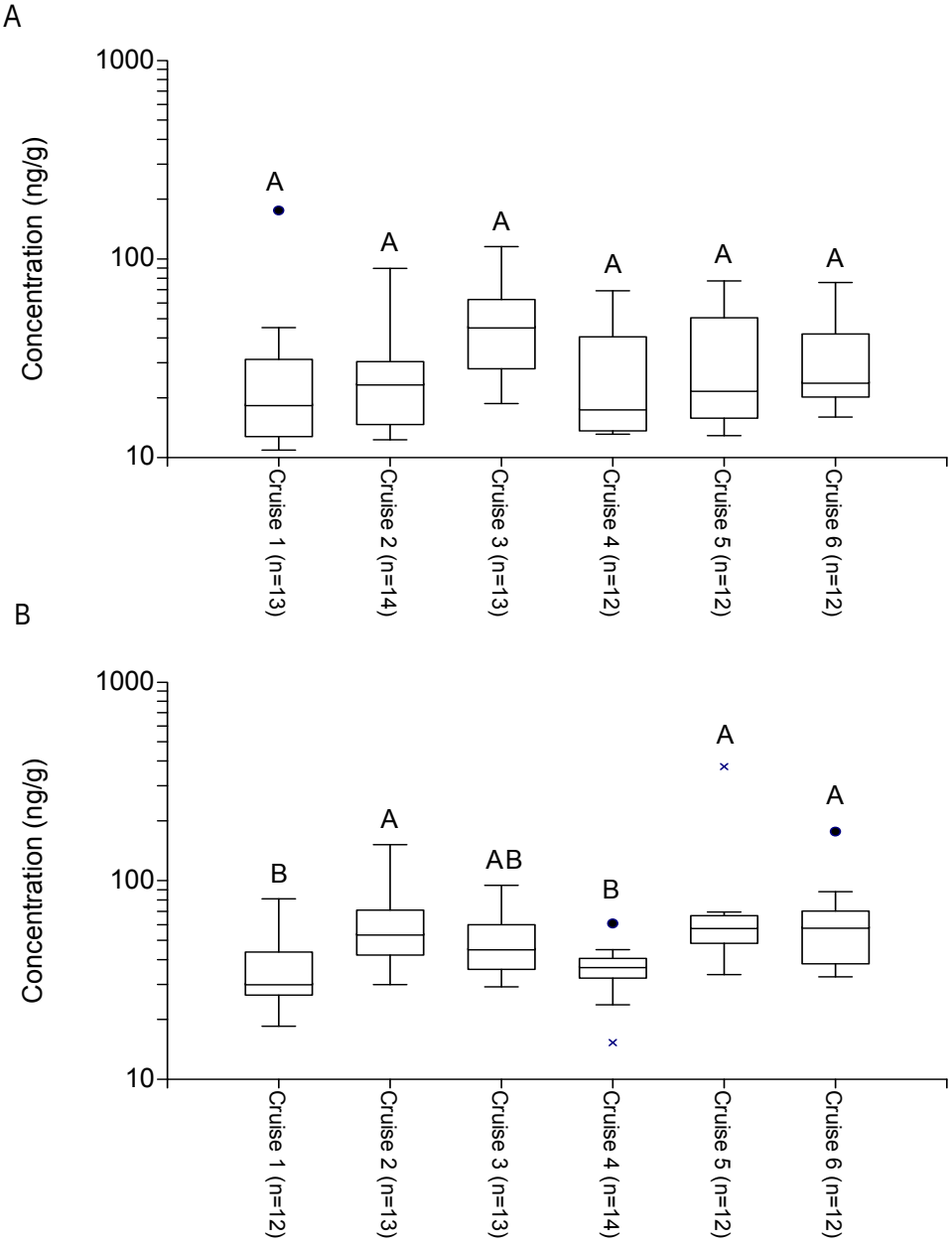
Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

7.1.2 Temporal Variation

Lake Michigan plankton were sampled in six separate cruises: June 1994, August 1994, September/October 1994, March/April 1995, August 1995, and September/October 1995. Two-way analysis of variance (accounting for cruise and sampling station) was conducted on log-transformed mercury data to evaluate temporal and geographical trends. This analysis revealed that total mercury concentrations in zooplankton differed significantly by cruise. In both sampling years, mercury concentrations in zooplankton were lowest in the spring (June 1994 and March/April 1995), peaked in late summer (August 1994 and August 1995), and remained elevated throughout the fall (September/October 1994 and September/October 1995) (Figure 7-2). In each year, mercury concentrations were significantly higher (at the 95% confidence level) in late summer than in the spring. Zooplankton mercury concentrations in the fall were also higher than spring amounts, but this difference was only significant for 1995 fall results (Cruise 6).

Phytoplankton mercury concentrations also differed significantly among cruises, based on the two-way analysis of variance, however, Tukey's multiple comparisons test did not identify any individual comparisons as significantly different. In both years, phytoplankton mercury concentrations increased throughout the summer and were highest in the fall. Individual differences between cruises, however, were not identified as statistically significant.

Figure 7-2. Mercury Concentrations in Phytoplankton (A) and Zooplankton (B) Measured in Lake Michigan during Six Cruises



(Cruise 1 = June 1994, Cruise 2 = August 1994, Cruise 3 = September/October 1994, Cruise 4 = March/April 1995, Cruise 5 = August 1995, and Cruise 6 = September/October 1995)

Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

7.1.3 Geographical Variation

Plankton samples were collected from 15 sampling stations in Lake Michigan (see Figure 2-7 in Chapter 2). Nine of these sampling stations were focused in the following four biological sampling areas or biota boxes:

- **Chicago biota box** — around Station 5 in the southern Lake Michigan basin near Chicago
- **Sturgeon Bay biota box** — a combination of three stations (110, 140, and 180) on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** — a combination of two stations (240 and 280) in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** — a series of three stations (310, 340, and 380) on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

In addition to focused sampling in these areas, samples also were collected from six LMMB monitoring sites throughout the lake (Table 7-1). Table 7-2 shows the concentrations of total mercury measured in plankton collected from the various sampling locations.

Considering all 15 individual sampling stations, two-way analysis of variance (accounting for cruise and sampling station) revealed no significant differences among sampling stations in phytoplankton or zooplankton mercury concentrations (Figure 7-3). When combining data within biota boxes, phytoplankton mercury concentrations still did not vary significantly among the biota box stations. The highest individual (176 ng/g) and mean (46.9 ng/g) phytoplankton mercury concentrations were observed at the Saugatuck biota box, but this site also contained the greatest variability, and differences between this site and other sites were not statistically significant (at the 95% confidence level).

Zooplankton mercury concentrations did vary significantly among biota boxes, however, no distinct trend was observed. A significant interaction occurred between the biota box and cruise variables, such that significant differences between stations were cruise-dependent. During Cruise 1, zooplankton mercury concentrations at the Saugatuck biota box were significantly higher than at the Sturgeon Bay biota box. During Cruise 3, zooplankton mercury concentrations at the Port Washington biota box were significantly higher than at the Saugatuck biota box. During Cruise 6, zooplankton mercury concentrations at the Chicago biota box were significantly higher than at the Saugatuck biota box.

7.1.4 Bioaccumulation

Mercury is known to accumulate in living organisms at levels far above concentrations in the water column. The degree of this accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

In the LMMB Study, bioaccumulation factors for mercury were calculated as the mean concentration of mercury in phytoplankton or zooplankton divided by the lake-wide mean concentration of total mercury in Lake Michigan. Concentrations of total mercury in Lake Michigan plankton were generally 10^5 times higher than total mercury concentrations in Lake Michigan water, which averaged 0.328 ng/L (or 0.000328 ng/g, assuming the density of water is 1 g/mL). Bioaccumulation factors from water to phytoplankton were 1.07×10^5 and from water to zooplankton were 1.66×10^5.

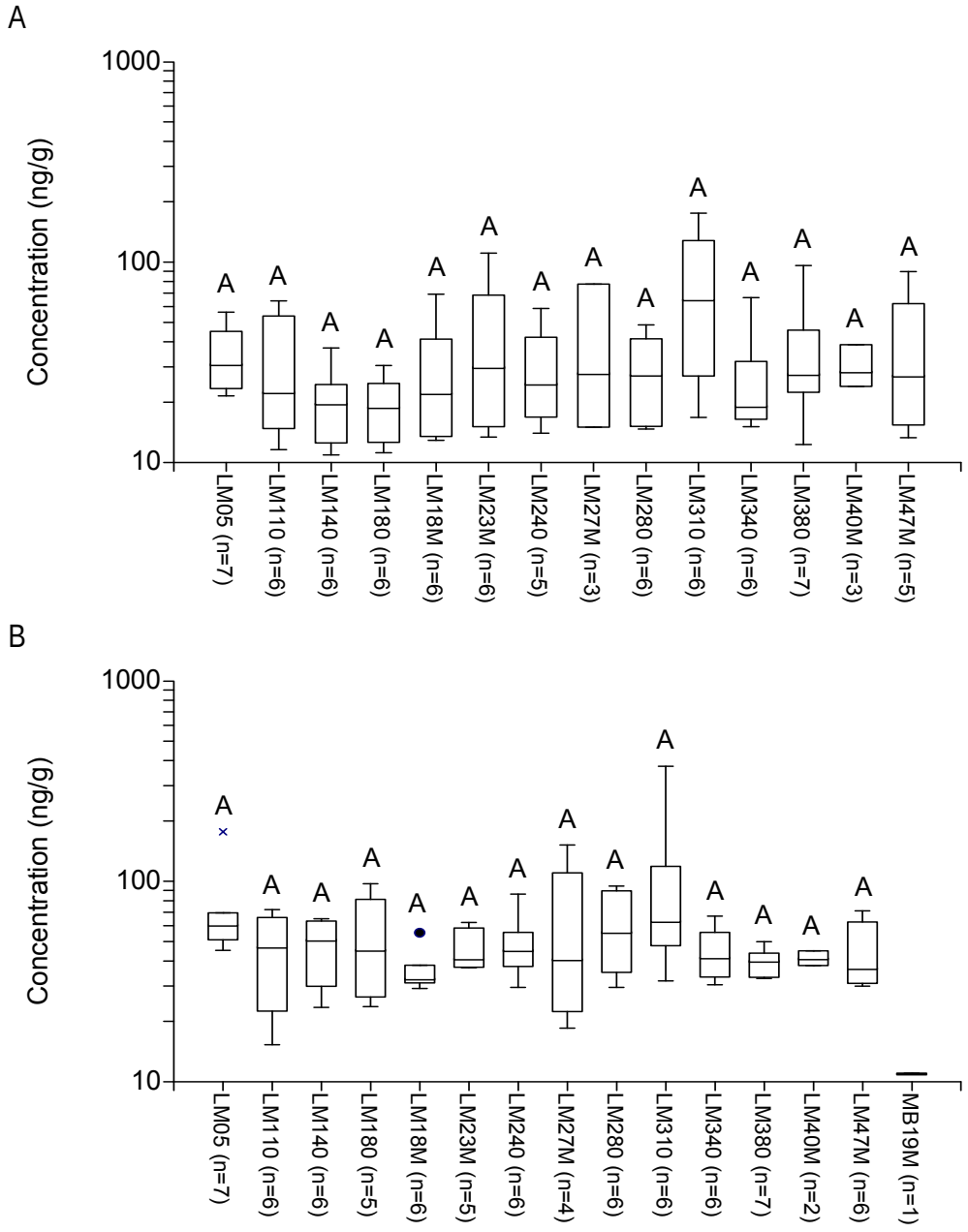
To evaluate the accumulation and transfer of mercury between trophic levels within the lower pelagic food web, biomagnification factors also were calculated. Biomagnification factors between primary producers and primary consumers were calculated as the concentration of contaminants in zooplankton divided by the concentration in phytoplankton. The biomagnification factor for mercury between phytoplankton and zooplankton was 1.55.

Table 7-2. Mercury Concentrations in Plankton Measured at Various Sampling Stations in Lake Michigan

Sample Type	Sampling Station		N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
	Biota Box	Station						
Phytoplankton	Chicago biota box	05	7	35.3	21.5 to 56.3	12.7	36.2	0
	Sturgeon Bay biota box	110	6	31.6	11.6 to 64.1	21.5	67.8	0
		140	6	20.4	10.9 to 37.3	9.31	45.7	0
		180	6	19.4	11.2 to 30.5	7.26	37.4	0
		combined	18	23.8	10.9 to 64.1	14.5	60.8	0
	Port Washington biota box	240	5	29.6	14.0 to 58.8	17.4	58.6	0
		280	6	28.8	14.7 to 48.7	13.3	46.3	0
		combined	11	29.2	14.0 to 58.8	14.5	49.6	0
	Saugatuck biota box	310	6	78.7	16.8 to 176	58.9	74.9	0
		340	6	27.0	15.1 to 66.6	19.7	72.9	0
		380	7	36.8	12.3 to 96.4	28.1	76.4	0
		combined	19	46.9	12.3 to 176	42.9	91.5	0
	Other	18M	6	29.4	12.9 to 69.2	21.3	72.6	0
		23M	6	44.2	13.4 to 111	37.7	85.2	0
		27M	3	40.2	15.0 to 77.7	33.1	82.2	0
		40M	3	30.4	24.0 to 38.7	7.53	24.8	0
		47M	5	38.2	13.3 to 89.9	31.0	81.2	0
Zooplankton	Chicago biota box	05	7	75.0	45.3 to 177	45.9	61.2	0
	Sturgeon Bay biota box	110	6	45.6	15.3 to 72.4	22.5	49.4	0
		140	6	47.8	23.5 to 65.1	16.7	34.9	0
		180	5	52.9	23.7 to 97.5	30.3	57.2	0
		combined	17	48.5	15.3 to 97.5	22.0	45.4	0
	Port Washington biota box	240	6	49.3	29.6 to 86.5	19.4	39.4	0
		280	6	60.5	29.6 to 94.8	26.9	44.5	0
		combined	12	54.9	29.6 to 94.8	23.1	42.1	0
	Saugatuck biota box	310	6	112	31.9 to 376	131	117	0
		340	6	44.7	30.5 to 67.2	13.5	30.1	0
		380	7	40.0	32.8 to 50.0	5.96	14.9	0
		combined	19	64.2	30.5 to 376	76.9	120	0
	Other	18M	6	36.0	29.2 to 55.4	9.65	26.9	0
		23M	5	46.7	37.1 to 62.4	11.4	24.5	0
		27M	4	63.1	18.5 to 152	60.2	95.4	0
		40M	2	41.5	38.0 to 45.0	4.95	11.9	0
		47M	6	44.5	30.0 to 71.3	17.2	38.6	0
		19M	1	11.0	NA	NA	NA	100

NA = Not applicable

Figure 7-3. Mercury Concentrations in Phytoplankton (A) and Zooplankton (B) Measured at Various Sampling Stations in Lake Michigan



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

7.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of method quality objectives (MQOs) for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of plankton mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 7-3 provides a summary of flags applied to the plankton mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. No results were qualified as invalid, thus all results are represented in the analysis of plankton mercury concentrations presented in this report.

Table 7-3. Summary of Routine Field Sample Flags applied to Mercury in Plankton Samples

Flag	Number of QC Samples	Percentage of Samples Flagged
EHT, Exceeded Holding Time	—	75% (118)
FBS, Failed Blank Sample	18 lab reagent blank samples	44% (69)
FDL, Failed Lab Duplicate	31 lab duplicate samples	0
FFD, Failed Field Duplicate	38 field duplicate samples	4% (6)
FLS, Failed Lab Spike	11 lab fortified spiked samples	0
SCF, Suspected Field Contamination	—	1% (2)
UDL, Below Sample-Specific Detection Limit	—	1% (1)

The most frequently applied data validation flag was for exceeding sample holding times. Seventy-five percent of samples were analyzed beyond the 420-day established holding time. The median holding time for frozen plankton samples was 614 days, and frozen samples were held as long as 896 days prior to mercury analysis. The MQOs for holding times were based on educated, conservative assessments by the PIs, however, the appropriateness of these holding times has not been rigorously determined and the effects of extended holding times have not been investigated in the plankton matrix. Because phytoplankton samples were analyzed for total mercury, as opposed to the determination of mercury

species, possible conversion of mercury among individual species during the extended holding times would not likely affect total mercury measurements and loss of mercury would likely be negligible.

Laboratory reagent blanks were analyzed to assess the potential for contamination of routine field samples. A total of 18 laboratory reagent blanks were analyzed, and 11 of these 18 blanks contained detectable mercury. Forty-four percent of routine field samples were associated with (e.g., analyzed in the same batch) one of these 11 blanks that contained detectable mercury and were flagged for a failed blank (FBS). While 44% of routine field samples were flagged for associated blank failure, the maximum level of mercury detected in laboratory reagent blank samples was 0.1 ng/g, which is 100 times less than the lowest measured mercury concentration in plankton samples (10.9 ng/g). For this reason, contamination is not believed to significantly affect the reported plankton mercury results.

In addition to laboratory reagent blanks, laboratory dry blanks were analyzed at a frequency of 1 per 12 routine field samples. These blank results were not used to flag data, because they were not linked to specific routine field samples. Like laboratory reagent blanks, measured concentrations in laboratory dry blanks were 0.1 ng/g or below, further indicating that contamination did not significantly affect reported plankton mercury results. While blank sample analysis indicates no pervasive contamination, two samples were flagged for suspected field contamination based on a hydraulic fluid spill on the deck of the sampling vessel during the June 1994 sampling at Station 310.

A total of 38 field duplicate samples and 31 laboratory duplicate samples were analyzed to assess precision. From each cruise (except the January 1995 cruise that visited only two sites), duplicate samples were collected at one to six stations. Laboratory duplicates were prepared at a frequency of at least 2 per set of 24 routine field samples. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD or FDL) if the relative percent difference between results for a sample and its duplicate was greater than 30%. No laboratory duplicates failed to meet this criteria, and only 6 of the 38 field duplicates were flagged.

Laboratory fortified spike samples were used to monitor analytical bias, and no results were qualified for failed laboratory spikes. Based on an analysis of laboratory spikes, standard reference material recovery, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 7-4 provides a summary of data quality assessments for several of these attributes for plankton data. The results of laboratory and field duplicate samples revealed good system and analytical precision for plankton data. The mean RPD for field duplicate samples was 19.8% and the mean RPD for laboratory duplicate samples was 11.2%.

Analytical bias was evaluated by calculating the mean recovery of a standard reference material (SRM) from the National Institute of Standards and Technology and the mean recovery of laboratory fortified spike samples (LFS). Results indicated very little overall bias for analytical results. Mean recoveries for SRM 1515, an apple leaf sample with a certified value of 0.044 mg/kg, were 98%, and mean LFS recoveries were 103%, just slightly above and below the ideal recovery of 100%.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the sample-specific detection limit. Only one sample, or 0.6% of the data, was below the detection limit. Results

from this sample were not censored and were used as reported in the analysis of plankton mercury data presented in this report.

Table 7-4. Data Quality Assessment in Plankton Samples

Parameter	Number of QC Samples	Assessment
Number of Routine Samples Analyzed	—	157
System Precision, Mean Field Duplicate RPD (%), >MDL	38 field duplicate pairs	19.8%
Analytical Precision, Mean Lab Duplicate RPD (%), >MDL	28 lab duplicate pairs	11.2%
Analytical Bias, Mean SRM (%)	18 SRM samples	98%
Analytical Bias, Mean LFS (%)	11 LFS samples	103%
Analytical Sensitivity, Samples reported as <MDL (%)	—	0.6%

MDL = Sample-specific Detection Limit
SRM = Standard Reference Material
LFS = Laboratory Fortified Spike

7.3 Data Interpretation

7.3.1 Mercury Levels in Lake Michigan Plankton

In the LMMB Study, plankton mercury levels ranged from 10.9 to 376 ng/g and averaged 35.0 ng/g in phytoplankton and 54.3 ng/g in zooplankton. This is very similar to the average phytoplankton and zooplankton mercury concentrations of 30 and 56 ng/g, respectively, measured by Watras and Bloom (1992) in one basin of Little Rock Lake, in north-central Wisconsin. Little Rock Lake is divided into two separate basins, one of which has been experimentally acidified. Watras and Bloom (1992) measured slightly higher mercury concentrations (average of 40 ng/g for phytoplankton and 75 ng/g for zooplankton) in the acidified basin, compared to the reference basin.

Higher plankton mercury levels were also measured in numerous Wisconsin, Minnesota, and Canadian lakes. In Devil's Lake, Wisconsin, Herrin *et al.* (1998) measured average methylmercury concentrations of 186 and 100 ng/g in *Daphnia* during 1994 and 1995, respectively. Sorenson *et al.* (1990) measured an average zooplankton mercury concentration of 90 ng/g across 65 Minnesota lakes. Similarly, Tremblay *et al.* (1995) measured an average mercury concentration in zooplankton of 107.6 ng/g across 73 Canadian lakes. Plankton mercury levels measured in these studies were generally two times the levels observed in Lake Michigan. This is likely due to higher mercury concentrations in the water of these lakes than in Lake Michigan. For instance, the average surface water mercury concentration in the 65 Minnesota lakes measured by Sorenson *et al.* (1990) was 2.47 ng/L. This is more than 7 times the average total mercury concentration of 0.328 ng/L measured in Lake Michigan during the LMMB Study. Similarly, water concentrations in Devil's Lake, Wisconsin exceeded 2 ng/L. For the 73 Canadian lakes, Tremblay *et al.* (1995) did not measure water column concentrations.

7.3.2 Seasonal Considerations

Zooplankton mercury levels measured in the LMMB Study were lowest in the spring and peaked in late summer. Phytoplankton mercury levels increased throughout the summer and peaked in the fall, however, individual differences between cruises were not statistically significant for phytoplankton mercury data. The seasonal patterns of plankton mercury concentrations observed in the LMMB Study also have been documented by other researchers. In 12 northern Minnesota lakes, Monson and Brezonik

(1998) observed seasonal variations in plankton mercury concentrations with the lowest values occurring in spring and increasing throughout the summer. Similarly, Kirkwood *et al.* (1999) observed increases in phytoplankton mercury concentrations in the hypolimnion throughout the summer season in two Canadian lakes. In Devil's Lake, Wisconsin, Herrin *et al.* (1998) noted that mercury concentrations in the water of the hypolimnion increased during stratification, and that mercury concentrations in *Daphnia* peaked near the time of lake turnover in the fall (Herrin *et al*., 1998). Concentrations of methylmercury in phytoplankton and zooplankton increased two to four-fold between peak stratification and complete mixing. Herrin *et al.* (1998) concluded that mercury (particularly methylmercury) stored in the anoxic hypolimnion during summer stratification is an important source of mercury to the food chain during turnover. While plankton mercury levels measured in the LMMB Study increased in the late summer and fall as described by Herrin *et al*. (1998) in Devil's Lake, water column concentrations in Lake Michigan did not follow the same trend. No seasonal differences in epilimnetic or hypolimnetic mercury levels were observed in the LMMB Study (see Chapter 5). The Lake Michigan main lake hypolimnion is always oxic.

7.3.3 Bioaccumulation and Biomagnification

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. Bioconcentration factors in phytoplankton and zooplankton from a north-central Wisconsin lake were approximately 3×10^4 and 5×10^4, respectively (Watras and Bloom, 1992). Similarly, bioaccumulation factors for plankton in 12 Minnesota lakes were approximately 3×10^4 (Monson and Brezonik, 1998).

In addition to bioaccumulation of mercury in the lower pelagic food web, 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. Other studies have also documented the biomagnification of mercury within the lower pelagic food web. Watras and Bloom (1992) measured higher mercury and methylmercury levels in zooplankton than phytoplankton in both reference and acidified lakes.

Tremblay *et al.* (1998) concluded biomagnification in the planktonic food web of Canadian reservoirs based on observed increases in methylmercury with increasing plankton size. Tremblay *et al.* (1998) measured biomagnification factors of 2.5 to 3 between adjacent trophic levels within the planktonic food web. These biomagnification factors are likely higher than those calculated for Lake Michigan because they are calculated based on methylmercury levels rather than total mercury levels.

While methylmercury concentrations were not measured in plankton and water during the LMMB Study, Watras and Bloom (1992) concluded that it is the methylmercury species that is most efficiently bioaccumulated and transferred up aquatic food chains. Methylmercury bioaccumulation factors were considerably higher (3×10^5 and 1×10^6 for phytoplankton and zooplankton, respectively) than bioaccumulation factors calculated based on total mercury concentrations. To further emphasize the importance of methylmercury in bioaccumulation and biomagnification, Back and Watras (1995) observed biomagnification of methylmercury from seston (which included phytoplankton and other organic suspended matter) to herbivorous zooplankton, but reported that total mercury levels did not increase between these trophic levels. Watras and Bloom (1992) also found that methylmercury becomes a progressively greater fraction of total mercury as trophic levels increase. For instance, 5% of total mercury in water was methylmercury; 13% of phytoplankton total mercury was methylmercury; 29% of zooplankton mercury was methylmercury; and >90% of fish mercury was methylmercury.

7.3.4 Other Interpretations and Perspectives

Researchers have identified various physical and chemical properties within studied lakes that have correlated with plankton mercury levels in the lakes. In general, mercury accumulation in plankton has been observed to increase with increasing water concentrations, and decreasing pH, however, researchers have not all agreed on the importance of these factors or additional factors in affecting bioaccumulation. Sorensen *et al.* (1990) found that concentrations of mercury in zooplankton from 80 northern Minnesota lakes correlated with mercury in water, mercury in fish, zooplankton density (negative correlation), pH (negative correlation), and total organic carbon. Westcott and Kalff (1996) found that water color and pH together were the best predictors of methylmercury levels in plankton from 24 Ontario lakes. Methylmercury concentrations also were positively correlated with drainage ratio and percent wetlands in the catchment (Westcott and Kalff, 1996). In contrast, Tremblay *et al.* (1995) found that zooplankton mercury concentrations in 73 Canadian lakes were poorly correlated with catchment area, primary production, total organic carbon, and sediment mercury levels. Monson and Brezonik (1998) found no correlations of plankton mercury levels with acid-neutralizing capacity, pH, dissolved organic carbon, sulfate, chlorophyll, or phosphorus in 12 northern Minnesota lakes. Back and Watras (1995) also found no relationship between total mercury in zooplankton and pH in 12 northern Wisconsin lakes.

In a direct comparison between the acidified and reference basins of Little Rock Lake, Watras and Bloom (1992) found that pH greatly influenced mercury accumulation, particularly in the methylmercury form. Mean concentrations of total mercury in phytoplankton and zooplankton were 20-30% higher in the acidified lake (pH 4.7) than in the reference lake (pH 6.1), and mean concentrations of methylmercury were 2-4 times higher in the acidified lake. The acidified conditions also appeared to greatly affect the fraction of mercury that is in the form of methylmercury. In the acidified lake, methylmercury comprised >90% of the total mercury in Cladocera, whereas <30% of total mercury in Cladocera from the non-acidified lake was methylmercury. Watras and Bloom (1992) concluded that it is the methylmercury form of mercury that is preferentially bioaccumulated and transferred up aquatic food chains, so greater proportions of methylmercury at lower trophic levels in the food chain will likely lead to greater biomagnification of mercury at higher levels of the food chain.

Later work by Watras *et al.* (1998) demonstrates that the bioaccumulation of mercury depends not only on the form of mercury under consideration (e.g., methylmercury versus inorganic mercury), but also on the particular chemical species within each form (e.g., "neutral" species such as CH_3HgCl^0 and CH_3HgOH^0 behave differently than ionized forms such as CH_3Hg^+). Some of the differences in bioaccumulation are a function of interactions and correlations with other water quality characteristics such as pH and dissolved organic carbon (DOC). The LMMB Study did not measure methylmercury in the water or all of the trophic levels of biota, nor were particular mercury species measured within any of the media. Therefore, it is unlikely that the results from this study can be used to delineate specific bioaccumulation mechanisms or pathways. Rather, the bioaccumulation factors reported in this chapter are relatively simple approximations of the transfer of mercury from the water column to the various trophic levels that are indicative of general trends in mercury concentrations.

Finally, the zooplankton data from Watras and Bloom (1992) represent results for organisms that were fractionated by size and sorted by species prior to analyses. Watras and Bloom (1992) contrast their results with bioaccumulation factors calculated from mixed assemblages of zooplankton, in which *"obscure small but important difference in bioaccumulation."* The plankton results from the LMMB Study are based on aggregate samples without regard for species. Thus, although the LMMB results demonstrate that there is bioaccumulation of mercury within the lower pelagic food web, the calculated bioaccumulation factors may not represent the accumulation that occurs between particular species within the lake ecosystem.

Chapter 8
Mercury in Fish

8.1 Results

Lake Michigan fish were collected from April 1994 through October 1995 for total mercury analysis (see Section 2.4.6 for details of the sample collection procedures and Section 2.5.5 for the details of the analysis procedures). Lake trout and coho salmon were collected using gill nets, trawl nets, or other appropriate means. Up to five individual whole fish of the same species and size or age category were combined to produce composite fish samples at each collection. Adult lake trout from 172 to 933 mm in length were collected from three biological sampling areas or biota boxes (see Figure 2-7 in Chapter 2):

- **Sturgeon Bay biota box** — a combination of three stations (110, 140, and 180) on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** — a combination of two stations (240 and 280) in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** — a series of three stations (310, 340, and 380) on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan

Coho salmon were collected in three distinct age classes (hatchery, yearlings, and adult). Coho salmon were collected from various sites selected to follow the seasonal migration of coho, which travel up Lake Michigan tributaries in the fall to spawn. During the summer, coho salmon were collected from the east central and west central regions of the lake. During the fall, coho salmon were collected from the northeastern side of the lake near the Platte River and on the western side of the lake near the Kewaunee River (see Figure 2-7 in Chapter 2). In addition, young coho salmon (hatchery) were collected directly from the Platte River hatchery, where the majority of Lake Michigan stocked salmon originate. Overall, a total of 201 composite samples of lake trout and coho salmon were collected and analyzed for total mercury by cold vapor atomic fluorescence spectroscopy (Table 8-1).

Table 8-1. Number of Composite Fish Samples Analyzed for Mercury

Species-Size Category	Sampling Dates	Number of Composite Samples
Coho-Hatchery	04/21/94 to 04/27/94	5
Coho-Yearling	10/18/94 to 11/16/94	8
Coho-Adult	05/10/94 to 10/25/94	32
Lake Trout	05/12/94 to 10/26/95	156
	Total	201

8.1.1 Variation Among Species

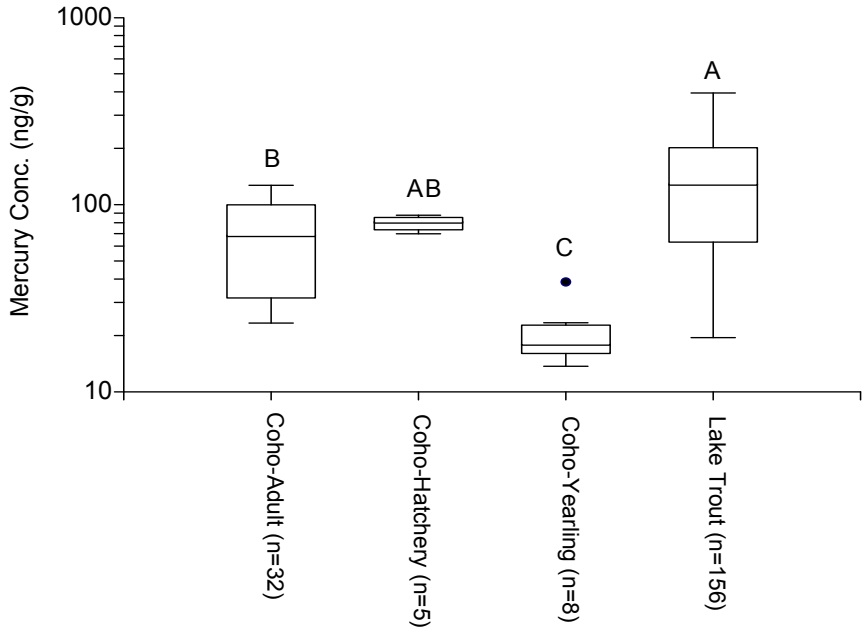
Table 8-2 shows the mean concentration of total mercury (on a wet-weight basis) in Lake Michigan coho salmon and lake trout. Mercury concentrations in adult lake trout ranged as high as 396 ng/g and averaged 139 ng/g. In coho salmon, mercury concentrations ranged as high as 127 ng/g and averaged 79.9, 20.6, and 69.0 ng/g in hatchery, yearling, and adult salmon, respectively. Analysis of variance revealed that mercury concentrations in lake trout were significantly higher than in adult or yearling coho salmon (Figure 8-1). Adult coho salmon also were significantly higher in mercury concentrations than yearling coho, which contained the lowest mean concentration of mercury (20.6 ng/g). Coho salmon collected directly from the hatchery surprisingly contained higher mercury levels (average of 79.9 ng/g) than yearling or adult coho salmon and were not significantly different from lake trout mercury levels.

This is surprising because smaller, younger fish generally contain lower levels of bioaccumulative contaminants than older, larger fish. Among adult coho salmon and lake trout, fish length was highly correlated with total mercury concentrations (see Section 8.1.2). Higher mercury concentrations in hatchery samples than in adult coho may be due to differences in exposures between the hatchery and Lake Michigan or differences in uptake and elimination rates between hatchery and adult fish. Also, given the smaller number of composites of hatchery and yearling salmon, the mean values calculated for these groups may be less representative of their respective populations than mean values calculated for adult salmon and lake trout.

Table 8-2. Mean Total Mercury Concentrations in Lake Michigan Fish (Wet-weight Basis)

Species/Size Category	N	Mean (ng/g)	Median (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Coho-Hatchery	5	79.9	81.2	70.0 to 88.0	6.77	8.48	0
Coho-Yearling	8	20.6	18.1	13.7 to 38.6	7.85	38.0	0
Coho-Adult	32	69.0	69.8	23.3 to 127	35.9	52.0	0
Lake Trout	156	139	130	19.5 to 396	83.8	60.1	0

Figure 8-1. Total Mercury Concentration (Wet-weight Basis) in Lake Michigan Fish



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The trends observed in fish mercury concentrations were the same on a dry-weight basis (Table 8-3). Lake trout contained the highest mercury levels, followed by hatchery, adult, and yearling coho salmon. As with wet-weight basis results, dry-weight mercury concentrations in lake trout were significantly higher than in adult or yearling coho salmon, and mercury concentrations in adult coho salmon were significantly higher than in yearling coho salmon.

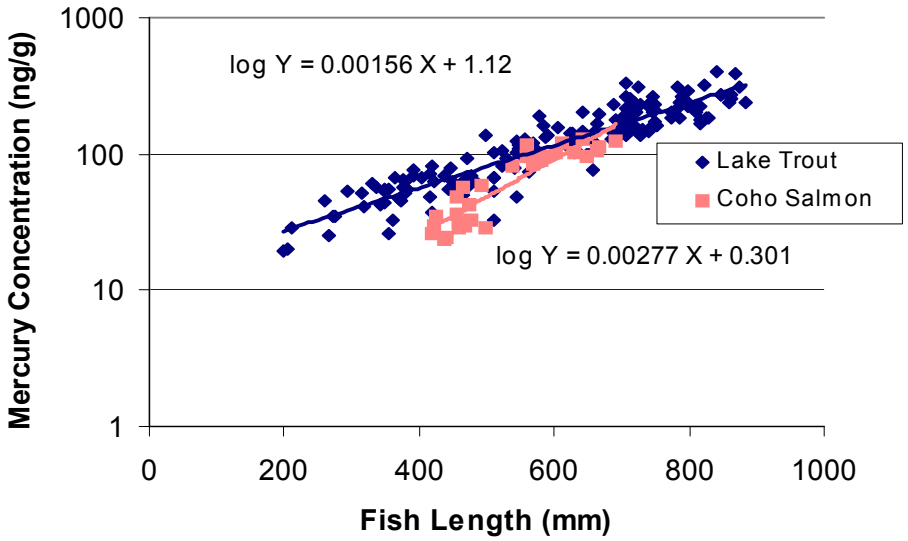
Table 8-3. Mean Total Mercury Concentrations in Lake Michigan Fish (Dry-weight Basis)

Species/Size Category	N	Mean (ng/g)	Median (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Coho-Hatchery	5	317	331	269 to 344	30.1	9.52	0
Coho-Yearling	8	71.3	57.4	43.1 to 156	36.2	50.7	0
Coho-Adult	32	248	255	98.8 to 504	119	47.9	0
Lake Trout	156	373	341	83.5 to 929	200	53.6	0

8.1.2 Factors Affecting Contaminant Concentrations

Log-transformed total mercury concentrations in Lake Michigan fish were highly correlated ($p<0.0001$) with fish length and lipid content. Fish length was positively correlated with adult lake trout and adult coho salmon mercury levels with r^2 values of 0.856 and 0.824, respectively (i.e., 85.6% and 82.4% of the variability observed in lake trout and adult coho salmon mercury concentrations are attributable to the fish length). It should be noted that the fish samples analyzed were composites of up to five individual fish. Correlations with fish length reflect the midpoint of the range of fish lengths that were incorporated into the composite sample. It is likely that correlations between contaminant concentrations and fish length would be stronger had contaminant concentrations been measured in individual fish samples, therefore allowing for direct comparison of length and contaminant concentration. Figure 8-2 shows the relationship between fish length and mercury concentrations in Lake Michigan lake trout and coho salmon. Mercury concentrations generally increased exponentially with increasing fish length, producing a linear relationship between fish length and log concentration. Because fish length is often used as a surrogate measure for fish age, this trend indicates either the increased accumulation of pollutants in older fish that have experienced longer duration exposures to mercury, or exposures to higher mercury concentrations.

Figure 8-2. Relationship of Fish Length and Mercury Concentration



Mercury concentrations in Lake Michigan fish also were strongly correlated with fish lipid content ($p<0.0001$). Lipid content was positively correlated with adult lake trout and adult coho salmon mercury levels with r^2 values of 0.684 and 0.531, respectively. This correlation, however, was likely due to the

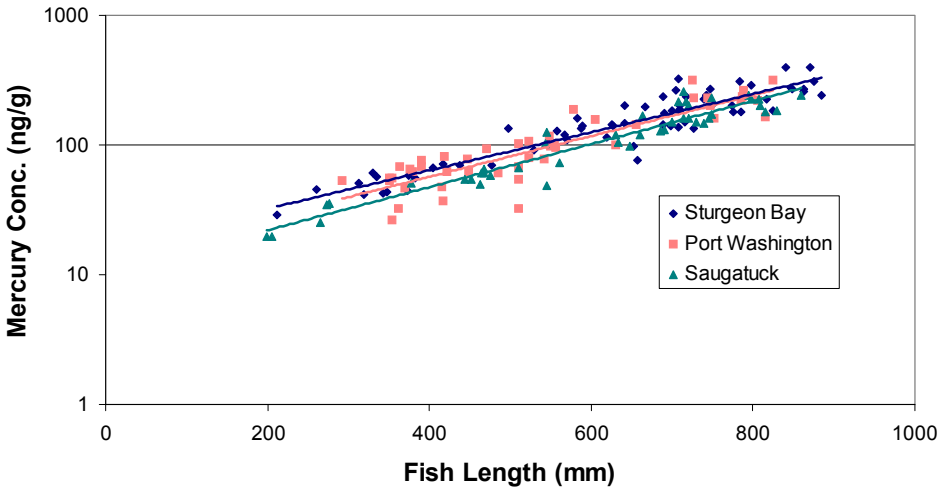
intercorrelation between fish length and lipid content. Lipid content was significantly correlated with fish length ($r^2 = 0.798$ for lake trout; $r^2 = 0.486$ for adult coho salmon), which was in turn correlated with mercury concentration. In general, mercury accumulation in fish is associated with proteins and storage in muscle tissue rather than storage in fatty tissues, where organic contaminants are accumulated, so lipid content is not considered a controlling variable in fish mercury concentrations. In the case of lake trout, multiple regression analysis supported the assumption that lipid content correlation with mercury concentration was a result of the intercorrelation between lipid content and fish length. Multiple regression analysis revealed that mercury concentrations in lake trout were not significantly affected by fish lipid content, when controlling for fish length. For adult salmon, however, multiple regression analysis revealed that mercury concentration was significantly affected by fish length, lipid content, and the interaction of these two factors.

8.1.3 Geographical and Seasonal Variation

Lake trout were collected from three biological sampling areas or biota boxes (Sturgeon Bay, Port Washington, and Saugatuck) during the spring, summer, and autumn months. Two-way analysis of variance (accounting for sampling station and season) revealed that mercury concentrations in lake trout did not differ significantly (at the 95% confidence level) among seasons but did differ significantly among biota boxes. This analysis was not conducted for coho salmon mercury data because coho were collected from various locations throughout the lake, rather than from the designated biota boxes, and coho composite samples occasionally consisted of fish from different sampling sites.

Mercury concentrations in lake trout from the three biota boxes averaged 165 ng/g at Sturgeon Bay, 114 ng/g at Port Washington, and 127 ng/g at Saugatuck. Tukey's multiple comparison test revealed that the mercury concentration in lake trout from Port Washington was significantly lower than in lake trout from Sturgeon Bay. This difference, however, is primarily due to differences in the size of fish collected from the sites. The length of lake trout from Port Washington averaged 536 mm, compared to an average of 629 mm for lake trout from Sturgeon Bay. Because fish mercury concentrations are so strongly correlated with fish length, decreased fish mercury concentrations at Port Washington could be due to the smaller size of fish from this site. Multiple regression analysis was used to evaluate differences between biota boxes while considering fish length. Figure 8-3 compares the mercury versus fish length regressions for fish collected at each of the biota boxes.

Figure 8-3. Total Mercury Concentrations in Lake Michigan Lake Trout of Various Sizes from the Three Biological Sampling Stations



While differences among biota boxes are small, multiple regression analysis determined that the regression intercept for Saugatuck is significantly lower than for the other two sampling locations. When comparing similarly sized fish from the three biota boxes, lake trout from Saugatuck contained significantly lower mercury concentrations than lake trout from Sturgeon Bay or Port Washington.

8.1.4 Bioaccumulation

Mercury is known to accumulate in living organisms at levels far above concentrations in the water column. The degree of this accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

In the LMMB Study, 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, which averaged 0.328 ng/L (or 0.000328 ng/g assuming a water density of 1 g/mL). 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. Bioaccumulation factors were not calculated for hatchery coho salmon, because these samples were not collected from Lake Michigan.

The fish species analyzed for mercury content in the LMMB Study (coho salmon and lake trout) represented only top predator fish species. While forage fish species were collected and analyzed for PCBs and *trans*-nonachlor, these species were not analyzed for mercury. For this reason, biomagnification of mercury in the upper pelagic food web could not be assessed. Biomagnification from the lower pelagic food web (plankton) to the upper pelagic food web (fish) is discussed in Chapter 9 of this report.

8.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of fish mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 8-4 provides a summary of flags applied to the fish mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. No results were qualified as invalid, thus all results are represented in the analysis of fish mercury concentrations presented in this report.

Table 8-4. Summary of Routine Field Sample Flags for Fish Mercury

Flag	Number of QC Samples	Percentage of Samples Flagged (%)
EHT, Exceeded Holding Time	—	0.5% (1)
FBS, Failed Blank Sample	44 lab reagent blank samples	0
FDL, Failed Lab Duplicate	153 lab duplicate groups	5% (10)
FMS, Failed Matrix Spike	9 lab matrix spike samples	0
FRS, Failed Lab Reference Sample	24 lab reference samples	0
FSR, Failed Standard Reference Material	24 standard reference material samples	1% (2)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

Few data quality flags were applied to fish mercury data. Of the 201 routine field samples analyzed for mercury, only 1 sample was flagged for exceeding sample holding time, 10 samples were flagged for failed laboratory duplicates, and 2 samples were flagged for a failed standard reference material. The one sample that was flagged for sample holding time exceeded the 1095-day criterion by 3 days. The average holding time for analyzed samples was 680 days.

Field duplicate samples could not be collected for the fish matrix, because individual fish are not expected to contain identical mercury concentrations. Laboratory duplicate samples, however, were prepared by subsampling collected fish samples. Of the 153 laboratory duplicate groups that were analyzed, only 10 exceeded the MQO of 25% relative percent difference (RPD). RPDs for these failed duplicate samples ranged from 25.2% to 31.3%.

A total of 44 laboratory reagent blanks were analyzed to assess the potential for contamination of routine field samples. All of these samples contained less than 1 ng mercury, so no samples were flagged for failed laboratory reagent blanks. Blank sample results ranged from 0 to 0.92 ng, which is more than 4 times below the lowest sample result of 4.1 ng. This indicates no significant contamination of routine field samples.

To evaluate the bias of analytical results, the laboratory analyzed matrix spike samples, laboratory reference samples that consisted of previously analyzed Lake Erie fish, and standard reference materials (SRM) from the National Institute of Standards and Technology. Two SRMs were used for this study: SRM 1566a, an oyster tissue sample with a certified value of 0.0642 mg/kg (no longer available) and SRM 1515, apple leaves, with a certified value 0.044 mg/kg.

No samples were flagged for failed matrix spikes or laboratory reference samples. Recoveries for matrix spike samples ranged from 82% to 109%. Recoveries for laboratory reference samples ranged from 90%

to 115%. Only one standard reference material sample, which was associated with two routine field samples, was flagged for recovery beyond the MQO of 80-120%. This sample achieved a recovery of 133%. Based on the analysis of laboratory matrix spike samples, laboratory reference samples, standard reference materials, laboratory reagent blank samples, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate groups. Table 8-5 provides a summary of data quality assessments for several of these attributes. The results of laboratory duplicate samples revealed good analytical precision for fish data. The mean RPD for laboratory duplicate samples was 11.7%.

Table 8-5. Data Quality Assessment for Mercury in Fish Samples

Parameter	Number of QC Samples	Assessment
Number of Routine Samples Analyzed	—	201
Analytical Precision, Mean Lab Duplicate RPD (%), >MDL	153 lab duplicate groups	11.7%
Analytical Bias, Mean SRM (%)	24 SRM samples	104%
Analytical Bias, Mean LMS (%)	9 LMS samples	92.8%
Analytical Bias, Mean LRS (%)	24 LRS samples	100%
Analytical Sensitivity, Samples reported as <MDL (%)	—	0%

Number of Sample/duplicate pairs used in the assessment is provided in parentheses
SRM = Standard Reference Material
LMS = Laboratory Matrix Spike
LRS = Laboratory Reference Sample

Analytical bias was evaluated by calculating the mean recovery of standard reference material samples (SRM), laboratory matrix spike samples (LMS), and laboratory reference samples (LRS). Results indicated very little overall bias for analytical results. Mean SRM recoveries were 104%, mean LMS recoveries were 92.8%, and mean LRS recoveries were 100%.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the method detection limit. No fish samples were below the detection limit of 0.1 ng/g. The lowest measured concentration in routine field samples was 13.7 ng/g, which is more than two orders of magnitude above the detection limit.

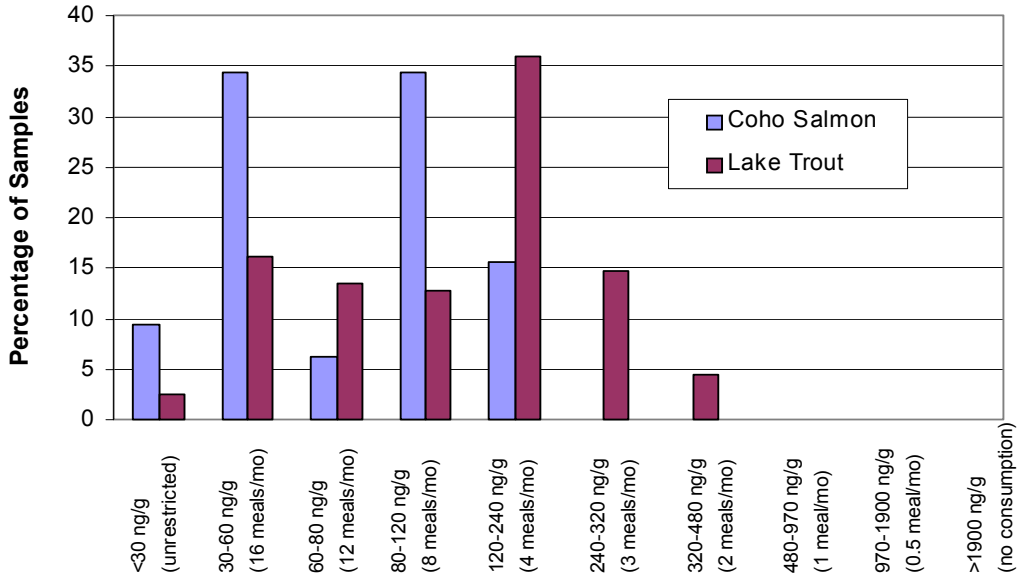
8.3 Data Interpretation

8.3.1 Comparison to Fish Advisory Levels

In the LMMB Study, mercury concentrations 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 content. Even the maximum mercury concentration measured in Lake Michigan fish during the LMMB Study (396 ng/g) was well below the FDA action level. While fish mercury concentrations measured in the LMMB Study do not exceed FDA action levels, these concentrations do warrant restrictions on fish consumption based on EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA, 2000).

Figure 8-4 shows the percentages of coho salmon and lake trout from the LMMB Study that fall into each of the advisory categories recommended by EPA for methylmercury contamination (USEPA, 2000). Since methylmercury was not measured in fish during the LMMB Study, samples were assigned to each category based on the conservative assumption that 100% of total mercury was in the form of methylmercury. Only 3% and 9% of lake trout and coho salmon, respectively, fell into the unrestricted consumption category. 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. For instance, Illinois has placed a state-wide methylmercury advisory of one meal per week of predator fish to protect sensitive populations (women of childbearing age and children). While Lake Michigan fish mercury concentration warrants 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.

Figure 8-4. Percentage of Lake Michigan Coho Salmon and Lake Trout Samples within each EPA-Recommended Fish Advisory Category



Fish advisory categories are based on EPA guidance (USEPA, 2000) and may vary by state. Fish advisory categories also are based on methylmercury concentrations, whereas the LMMB Study data represent total mercury concentrations. LMMB data were assigned to each category based on the conservative assumption that methylmercury contributes 100% of total fish mercury concentrations. Concentrations of mercury were converted to concentrations of methylmercury by multiplying by the ratio of the molecular weights for each mercury species (i.e., 215.625/200.59).

8.3.2 Regional Considerations

Mercury concentrations measured in top predators during the LMMB Study were similar to concentrations measured by other researchers in top predators from the Great Lakes. Rohrer *et al.* (1982) measured mercury concentrations of <100 to 350 ng/g in coho salmon from Lake Michigan tributaries. This is higher than measured in coho salmon during the LMMB Study but is consistent with concentrations measured in the other top predator species (i.e., lake trout). In Lake Ontario, Borgmann and Whittle (1991) found similar mercury concentrations in lake trout. Borgmann and Whittle (1991)

reported an average mercury concentration of 120 ng/g in lake trout collected in 1988. Borgmann and Whittle (1991) also reported that mercury concentrations in Lake Ontario lake trout had decreased steadily to this level from an average of 240 ng/g in 1977. Cappon (1984) measured similar total mercury levels in Lake Ontario lake trout fillets, but much higher concentrations in coho salmon fillets. Mercury concentrations in lake trout fillets ranged from 160 to 290 ng/g and averaged 230 ng/g. Mercury concentrations in coho salmon fillets ranged from 220 to 800 ng/g and averaged 420 and 460 ng/g in two separate fillet cross-sections.

Mercury concentrations of top predators from Lake Michigan were generally lower than those from smaller inland lakes. In a 1999 EPA report on fish mercury data from 1990 to 1995, the weighted mean concentration of mercury in walleye from lakes across Michigan was 375 ng/g (USEPA, 1999b). In a survey of 80 northern Minnesota lakes, Sorensen *et al.* (1990) measured an average mercury concentration of 450 ng/g (range 140 to 1500 ng/g) in a standard 550 mm northern pike. Rose *et al.* (1999) measured an average mercury concentration of 390 ng/g in largemouth bass from 24 lakes in Massachusetts. In a study of 219 Wisconsin lakes, average concentrations of mercury in 450 to 500 mm walleye ranged from 390 to 830 ng/g, depending upon the acid neutralizing capacity of the lakes (Lathrop *et al.*, 1991).

Mercury concentrations in forage fish species were not analyzed in the LMMB Study, so mercury biomagnification within the upper pelagic food web could not be documented. Mercury concentrations measured in top predator species during the LMMB Study, however, were higher than for forage fish species measured by other researchers. Brazner and DeVita (1998) measured mercury concentrations of 9.4 to 31 ng/g in young-of-the-year yellow perch from Green Bay. Mercury concentrations in young-of-the-year spottail shiners from Green Bay ranged from 10.5 to 33.5 ng/g. These concentrations are from 2 to 15 times lower than average mercury concentrations measured in top predators. Similarly, Borgmann and Whittle (1992) measured mercury levels of 37 ng/g and 32 ng/g in 1988 from Lake Ontario smelt and slimy sculpin, respectively.

8.3.3 Factors Affecting Contaminant Concentrations

In the LMMB Study, fish mercury concentrations varied primarily by species and by fish length. Lake trout contained significantly more mercury than coho salmon, and for both species, mercury content increased with fish length. Regression equations to describe mercury content based on the length of Lake Michigan lake trout and coho salmon were calculated, with r^2 values of 0.856 and 0.824, respectively. This correlation with fish length has been well documented and is the basis for size-specific fish advisories. Higher mercury concentrations are accumulated in larger fish because these fish are generally older and have experienced longer exposure durations to environmental concentrations, giving them more time to accumulate pollutants that are not easily degraded or eliminated.

In investigating fish mercury levels in a wide variety of lakes, researchers have identified other lake-specific factors that influence mercury concentrations in fish. Sorensen *et al.* (1990) found that mercury levels in northern pike from Minnesota lakes were correlated with mercury in water, mercury in zooplankton, total organic carbon, iron, and pH (negative correlation). In a study of 219 Wisconsin lakes, concentrations of mercury in walleye increased with increasing fish length and with decreasing acid neutralizing capacity (Lathrop *et al.*, 1991). Mean mercury concentrations ranged from 180 ng/g in the smallest walleye (250 to 349 mm) from high acid neutralizing capacity lakes (>1500 μeq/L) to 1470 ng/g in the largest walleye (>650 mm) from low acid neutralizing capacity lakes (<100 μeq/L). Rose *et al.* (1999) measured fish mercury levels in 24 Massachusetts lakes. Mercury concentrations in top predators (largemouth bass) were positively associated with fish weight, lake size, and watershed characteristics. Lake pH was not correlated with mercury concentrations in largemouth bass, but was correlated with mercury concentrations in brown bullhead and yellow perch.

Chapter 9
Cross-Media Interpretations

9.1 Summary of Mercury Concentrations in Lake Michigan Compartments

Mercury was found throughout the Lake Michigan ecosystem, with concentrations measured in air, water, sediment, tributaries, plankton, and fish samples collected from in and around the lake. Mercury was found in the majority of samples at levels above the corresponding detection limit for each ecosystem compartment (Table 9-1). Other than one sediment sample and one plankton sample, total mercury was detected in every sample in all media other than the open-lake water column. A total of 8 particulate mercury samples and 4 total mercury samples in the open-lake water column did not contain detectable levels of mercury. Comparisons of these frequencies should be done with care, due to the different types of detection limits used in the different mercury data sets. The type of detection limit used for the atmospheric phase or analytical fraction was described by the PI responsible for the analyses. Samples were only analyzed for methylmercury in the tributary compartment, and methylmercury was detected at levels above the MDL for the majority of the tributary samples. Approximately 15% and 3% of the dissolved and total samples, respectively, did not have detectable levels of methylmercury.

Table 9-1. Summary of Samples from each Ecosystem Compartment with Detectable Levels of Mercury

Ecosystem Compartment	Atmospheric Phase or Analytical Fraction	Detection Limit Type	% Samples with Mercury Above Detection Limit
Atmosphere	Vapor	System Detection Limit	100%
	Particulate	System Detection Limit	100%
	Precipitation	Method Detection Limit	100%
Tributary	Dissolved	Method Detection Limit	100%
	Total	Method Detection Limit	100%
Tributary Methylmercury	Dissolved	Method Detection Limit	85%
	Total	Method Detection Limit	97%
Open Lake	Particulate	Daily Detection Limit	92%
	Total	Daily Detection Limit	96%
Sediment	Total	Sample-Specific Detection Limit	99.5%
Plankton	Total	Sample-Specific Detection Limit	99%
Fish	Total	Method Detection Limit	100%

Vapor-phase mercury concentrations averaged from 2.06 to 3.62 ng/m^3 at five different shoreline and out-of-basin stations. The highest concentrations of vapor-phase mercury were detected at the IIT Chicago station, at the southern end of Lake Michigan. Particulate-phase mercury concentrations were lower than vapor-phase concentrations, with means ranging from 12.1 pg/m^3 to 73.7 pg/m^3. At individual stations, the mean vapor-phase concentration was 49 to 175% greater than the mean particulate-phase concentration. As with the vapor phase, the higher particulate-phase mercury concentrations were found at the IIT-Chicago site. Mean precipitation-phase mercury concentrations ranged from 15.2 to 26.1 ng/L. When calculated by weighting the concentrations according to the sample volume, mean precipitation-phase mercury concentrations ranged from 11.0 to 21.1 ng/L. As with the other two atmospheric phases, the highest mean concentration in the precipitation phase was measured at the IIT Chicago station.

Total mercury concentrations in Lake Michigan tributaries averaged from 1.07 to 28.9 ng/L, and dissolved mercury concentrations averaged from 0.666 to 3.71 ng/L. When calculated using the

differences between total mercury and dissolved mercury concentrations in individual samples, mean particulate mercury concentrations averaged from -0.0058 to 25.8 ng/L. In all cases, the highest mean concentrations were measured in the Fox River, a tributary that empties into Green Bay. The Fox River watershed is highly industrialized, and is suspected of being impacted by resuspension of contaminated sediments from legacy sources (Hurley *et al.*, 1998a; Rossmann and Edgington, 2000). Generally, among the other tributaries, mercury levels were higher in more urban/industrialized areas, and lower in primarily agricultural/forested areas.

Within the open-lake water column, total mercury concentrations averaged from 0.25 to 0.78 ng/L, and particulate mercury concentrations averaged from 0.029 to 0.17 ng/L. Generally, mercury was well mixed in the water column, as there was little variability in concentration among stations. While there was a slightly greater concentration of particulate mercury in Green Bay, there was no corresponding increase of total mercury.

The mean mercury concentration measured in precipitation samples was approximately 2.6 times greater than the mean total mercury concentration measured in the tributaries. With the exception of the Fox River tributary, all mean precipitation-phase mercury concentrations were greater than the mean total mercury concentration at any tributary. The mean mercury concentration in the Fox River was greater than the mean concentration in precipitation at any of the atmospheric stations. The overall mean precipitation-phase and tributary concentrations were 64 and 24 times greater than the mean total mercury concentration in the water column, respectively.

Total mercury concentrations measured in surficial sediments ranged from 0.002 to 0.26 mg/kg. Higher levels of mercury tended to accumulate in the sediments in deeper locations of the lake. Net fluxes of mercury ranged from 0.85 to 21 ng/cm^2/y and were highest along the eastern shore in response to the dominant water currents in the lake. Additional samples were collected from five different sediment trap stations, including two which were set at two different depths. Mean mercury concentrations for the different trap stations and depths ranged from 0.21 to 28 mg/kg. The highest mercury concentrations were found in samples collected from traps located in the southern basin of Lake Michigan. Both mercury concentrations and fluxes to surficial sediments have decreased since the 1970s.

9.2 Mercury Speciation

As discussed in Section 2.1.6 of this report, the organic compounds methylmercury and dimethylmercury have a greater toxicity than inorganic mercury, given equivalent doses. Methylmercury is generally the dominant form of mercury in higher levels of the aquatic food web. Methylmercury usually forms through methylation of inorganic mercury by bacteria in sediments or in the water column. Therefore, although atmospheric deposition and tributary flows are major sources of inorganic mercury to the lake, they may not be major sources of methylmercury.

Among the ecosystem components in Lake Michigan from which mercury samples were collected, methylmercury samples were collected from only the tributary component. While total mercury levels were greatest from the Fox River, and other tributaries located near urban/industrial sources, this was not the case for methylmercury. Tributaries located in mostly agricultural and forested areas such as the Menominee and Muskegon rivers had among the highest methylmercury concentrations. The Grand Calumet River, which had one of the highest mean total mercury concentrations and is located near the Chicago/Gary urban area, had the lowest mean methylmercury concentration.

The relative contribution of methylmercury to the total mercury concentrations measured in the tributaries was evaluated by calculating the percentage of the mean methylmercury concentration to the mean total

mercury concentration in each tributary. The percentage of mean methylmercury concentration to mean total mercury concentration ranged from 0.48% to 21% in the 11 tributaries. The 21% figure was for the Muskegon River, and the percentage contributions for the other 10 tributaries were all less than 6%. These lower percentages are consistent with other estimates of the contribution of methylmercury to total mercury in the water column (USEPA, 1997b), which indicate that methylmercury constitutes less than 10% of the total mercury concentration in water samples.

The percentage of methylmercury is greater in plankton and fish than in water samples. For example, Watras and Bloom (1992) measured both methylmercury and total mercury in various trophic levels in a basin of the Little Rock Lake, Wisconsin. Little Rock Lake is in north-central Wisconsin, in a relatively remote area with no industrial activity, and with restricted public-access. The lake is fed by groundwater and is used as an experimental lake. The lake has been artificially divided into two basins, one of which is acidified relative to the rest of the lake.

Watras and Bloom (1992) found that the percentage of methylmercury to total mercury in the water column and biota varied with pH as shown in Table 9-2, below.

Table 9-2. Percent of Mercury Attributable to Methylmercury in Little Rock Lake

	% Methylmercury of the Total Mercury	
Ecosystem Component	Reference Basin (pH = 6.1)	Acidified Basin (pH = 4.7)
Water column	5	12
Phytoplankton	13	31
Zooplankton	29	91
Fish	>90	>90

Both basins of the experimental lake were acidic, with a pH of 4.7 in the acidified basin, and 6.1 in the reference basin. In contrast, the mean pH measured in Lake Michigan for the LMMB Study was 8.2. Mason and Sullivan (1997) and Sullivan and Mason (1998) reported methylmercury concentrations in Lake Michigan that ranged from the detection limit of 5 pg/L to 42 pg/L, with an epilimnetic mean of 6 pg/L for August 1994 and 8.2 for October/November of 1994. (When calculating the mean, the detection limit of 5 pg/L was substituted for any sample result below the detection limit.) The hypolimnetic mean for August 1994 was 8 pg/L; whereas, the hypolimnetic concentrations for two samples in October/ November 1994 were 17 and 42 pg/L. These concentrations represent 2-3% of the mean total mercury concentration (Sullivan and Mason, 1998), which are lower than those reported by Watras and Bloom (1992).

A subsequent study of small lakes in northern Wisconsin by Watras *et al.* (1998) included the two basins of Little Rock Lake and 13 others lakes. The majority of these lakes are precipitation-domination seepage lakes in which the flows are dominated by precipitation, rather than riverine flow. Watras *et al.* (1998) measured the concentrations of total mercury, dissolved mercury, total methylmercury, and dissolved methylmercury in samples of dissolved organic carbon (DOC), microseston, zooplankton, and small fish. The microseston in the lakes in that study primarily consists of phytoplankton, bacterioplankton, and cellular debris. The zooplankton were collected in 153-μm mesh nets (a slightly larger mesh than used in the LMMB Study). It total, 727 yellow perch (*Perca flavescens*) and 139 golden shiners (*Notemigonus crysoleucas*) were collected during the spring and summer of 1994, ranging from one to seven years in age. Total mercury and total methylmercury were also measured in surficial sediments collected from these lakes.

Watras *et al.* (1998) reported the percentage of methylmercury relative to the total mercury concentration in the DOC, microseston, zooplankton, and small fish, as shown in Table 9-3. The mean pH of the lakes

on the study was 6.25, slightly higher than the reference basin in Little Rock Lake, and still well below the mean pH of 8.2 in the LMMB Study.

Table 9-3. Percent of Mercury Attributable to Methylmercury in 15 Lakes in Northern Wisconsin

Ecosystem Component	% Methylmercury of the Total Mercury
Dissolved organic carbon	11%
Microseston (includes phytoplankton)	18%
Zooplankton	57%
Fish	95%

Except for the fish, the percentages of methylmercury in Table 9-3 are intermediate to the results for the two basins on Little Rock Lake shown in Table 9-2. The results for the fish are comparable to those in Table 9-2, where the fish are listed as ">90%."

There has been one report of methylmercury in Lake Michigan sediments. Rossmann *et al.* (2001) reported methylmercury results for surficial sediments samples from Lake Michigan that were originally collected in 1994 - 1996 as part of the LMMB, but not analyzed for methylmercury as part of this study. The methylmercury concentrations ranged between 0.16 and 1.7 ng/g, with a mean and median of 0.57 and 0.45 ng/g, respectively. The methylmercury concentration varied between 0.11 and 1.4% of the total mercury concentration. The mean and median fraction of methylmercury were 0.42 and 0.35%, respectively.

The results from Watras *et al.* (1998) for methylmercury in surficial sediments of the lakes in northen Wisconsin are slightly higher than those from Rossmann *et al.* (2001), with a range of 0.5 to 7.4 ng/g, with a mean of 2.6 ng/g. The methylmercury concentration varied between 0.5 and 3.9% of the total mercury concentration, with a mean fraction of methylmercury of 1.5%.

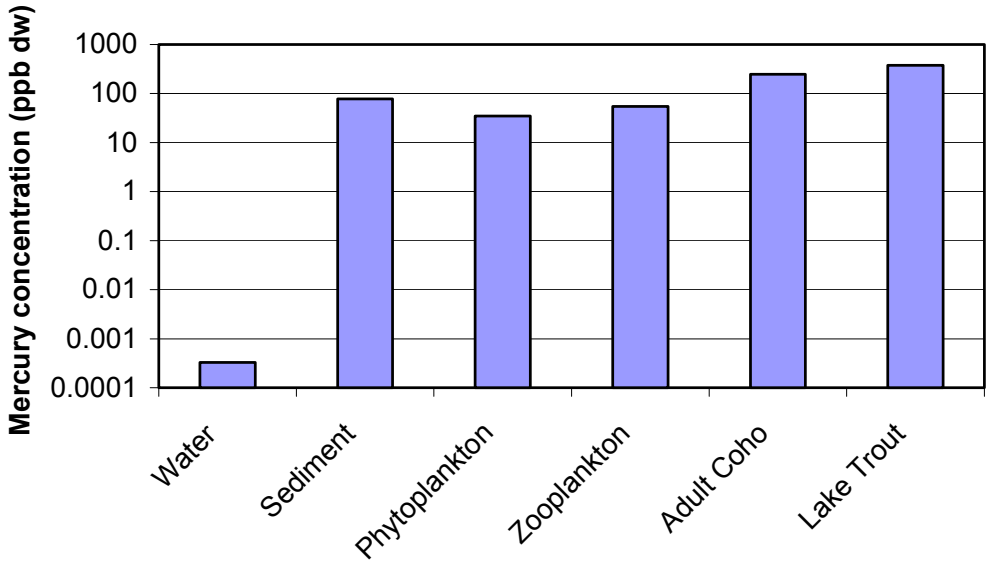
Studies comparing methylmercury and total mercury levels in fish have consistently shown that the majority of the measured total mercury consists of methylmercury. Herrin *et al.* (1998) measured mercury in bluegill and shiners in Devil's Lake, Wisconsin, and found that methylmercury accounted for nearly all of the total mercury in both species. However, they also found that methylmercury accounted for 26% to 58% of total mercury in open water, higher than most estimates. Rossmann *et al.* (2003) reported mean total and methylmercury concentrations in forage fish to be 0.051 and 0.34 mg/kg, respectively with methylmercury concentrations accounting for 60 and 91% of the total mercury for various species. Francis *et al.* (1998) also measured methylmercury and total mercury in various fish species in an estuary of Lake Erie. While mercury concentrations were frequently below detection limits, the percentages attributable to methylmercury were usually greater than 90% in common carp and channel catfish.

Unlike the two studies described above, Cappon (1984) measured methylmercury and total mercury in lake trout and coho salmon in Lake Ontario, allowing greater comparability with the LMMB Study. On average, methylmercury accounted for 71% of total mercury in both lake trout and coho salmon, a much lower percentage than those observed in the other studies. The levels of total mercury in lake trout in Lake Ontario were slightly higher, with a mean of approximately 165 ng/g on a wet-weight basis, compared to 139 ng/g in the LMMB Study. The levels of total mercury in Lake Ontario, however, were much higher, with a mean of approximately 240 ng/g, compared to 69 ng/g in the LMMB Study. Therefore, it is unclear whether the percentages of methylmercury from the study in Lake Ontario were unusually low due to taxonomic differences, or due to unusually high total mercury results.

9.3 Bioaccumulation and Biomagnification

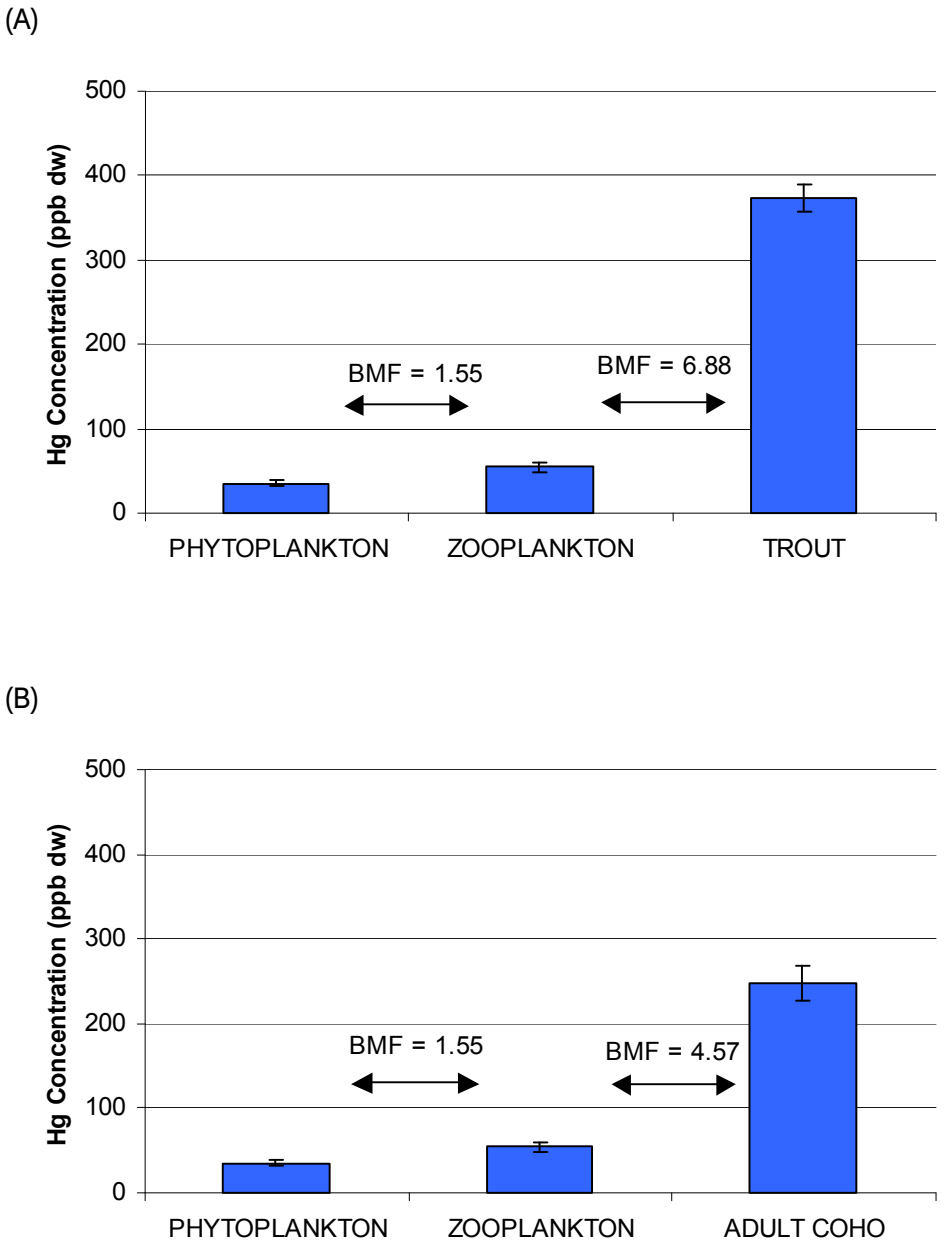
Mean mercury concentrations in the biota and mean concentrations in the water column and surficial sediments are presented in Figure 9-1. Within living components of the Lake Michigan ecosystem, mercury accumulated at concentrations higher than in any abiotic ecosystem component, with the exception of surficial sediments. Bioaccumulation factors for mercury ranged from 1.1×10^5 in phytoplankton to 1.1×10^6 in lake trout.

Figure 9-1. Mercury Concentrations in Various Components of the Lake Michigan Ecosystem



In addition to accumulating in living tissue at concentrations above those in the water, mercury also was magnified within the Lake Michigan food web (Figure 9-2). Total mercury concentrations increased from 35 ng/g in phytoplankton to 55 ng/g in zooplankton, a factor of 1.55. While samples of forage fish were not initially analyzed for mercury in the LMMB, an approximate two-step biomagnification factor can be calculated between zooplankton and the predator fish. The mean dry-weight mercury concentration in adult coho was 248 ng/g, and the mean mercury concentration in lake trout in adult coho was 373 ng/g. These concentrations correspond to biomagnification factors of 4.57 and 6.88, compared to zooplankton, respectively. From the bottom of the food web (phytoplankton) to the top of the food web (lake trout), mercury concentrations increase by a factor of 10.7.

Figure 9-2. Biomagnification Factors for Mercury in Lake Trout (A) and Adult Coho (B)



Because forage fish samples were not analyzed for mercury, biomagnification of mercury in the upper pelagic food web could not be estimated and compared to that calculated in total PCBs and *trans*-nonachlor (USEPA, 2003). However, biomagnification factors between zooplankton and predator fish species were much lower than those calculated for PCBs and *trans*-nonachlor. For total PCBs the biomagnification factor between zooplankton and *Mysis* was 1.5, and the factor between *Mysis* and lake trout was 31, yielding an estimated factor of 46.5 between zooplankton and lake trout. Similarly, the biomagnification factor between zooplankton and *Mysis* for *trans*-nonachlor was 1.6 and the factor between *Mysis* and lake trout was 19, yielding an estimated factor of 30.4 between zooplankton and lake trout. These factors were much larger than the corresponding factor of 6.88 for mercury. The biomagnification factor between phytoplankton and zooplankton was also smaller for mercury, at 1.55, compared to 3.4 for total PCBs and 9.5 for *trans*-Nonachlor.

The biomagnification of mercury in Lake Michigan occurred at a higher rate compared to previous studies in other lakes. For example, Herrin *et al.* (1998) measured a biomagnification factor for mercury of 2.7 between *Daphnia* and bluegills in Devil's Lake, Wisconsin in 1994 and 1995. The mean dry-weight total mercury concentrations measured in bluegills in Devil's Lake were 575 ng/g in 1994 and 324 ng/g in 1995. These levels are comparable with the mean of 373 ng/g measured in Lake Michigan in this study. The smaller biomagnification factor from Devil's Lake was likely due to greater mercury concentrations in the *Daphnia* compared to the zooplankton in Lake Michigan and the fact that bluegills are a step lower in the food chain than lake trout.

While mean total mercury concentrations were not reported for *Daphnia* in Devil's Lake, the mean methylmercury concentrations of 186 and 100 ng/g in 1994 and 1995 were 3.38 and 1.82 times greater than the mean total mercury concentration in zooplankton in Lake Michigan. The open-water total mercury concentrations were also greater in Devil's Lake, with a mean of 3.0 ng/L total mercury, almost an order of magnitude greater than the mean concentration observed in Lake Michigan. In addition, the biomagnification factors calculated in Devil's Lake were based on methylmercury, not total mercury. While the total mercury and methylmercury levels were comparable in that study, total mercury levels may have been considerably greater in *Daphnia* than the measured methylmercury concentrations, which would yield a biomagnification factor which would be greater than one calculated based on total mercury. For example, Watras and Bloom (1992) found that 29% of zooplankton mercury in Little Rock Lake, WI was methylmercury; whereas >90% of total mercury measured in fish was methylmercury. The comparability of the two studies may also be affected by the taxonomic differences of the sampled fish. Bluegills tend to be smaller than trout and will likely be lower on the food web than lake trout. In an EPA survey of mercury concentrations of fish (USEPA, 1999b), bluegills were found to have lower concentrations than most other fish species from which samples were collected, including largemouth bass, walleye and northern pike. Bluegill caught in Wisconsin for this survey had comparable mercury concentrations to those measured in Devil's Lake.

Francis *et al.* (1998) also found evidence of mercury biomagnification in Old Woman Creek, an estuary of Lake Erie. However, bioaccumulation and biomagnification factors could not be calculated, due to the prevalence of open-water, plankton, and fish samples without detectable levels of mercury. The detection limits reported in that study were higher than those for the LMMB Study, by up to two orders of magnitude in water and fish tissue samples. While mercury was also not detected in zooplankton samples, the detection limits for plankton samples in the two studies were comparable. However, the authors did conclude that bioaccumulation was occurring, based on higher levels of mercury, and greater rates of detection, in predatory catfish and bowfin.

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