Mercury in the Grand Calumet River/ Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001 and May 2002

By Martin R. Risch

Prepared in cooperation with the Indiana Department of Environmental Management

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Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
pound (lb)	0.4536	kilogram (kg)
micrometer (μm)	0.000039	inch (in.)
square meter (m^2)	10.76	square foot (ft^2)
gram per year (g/yr)	0.03527	ounce per year (oz/yr)
milligram (mg)	0.00003527	ounce (oz)
milligram per hour (mg/hr)	0.00003527	ounce per hour (oz/hr)
nanogram (ng)	0.00000003527	ounce (oz)
nanogram per square meter (ng/m^2)	0.0000003795	ounce per square foot (oz/ft^2)

Temperature is given in degrees Celsius (C), which may be converted to degrees Fahrenheit (^oF) as follows:

$$^oF = 1.8 \times {}^oC + 32$$

Vertical Datum: In this report, vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Abbreviated concentration units used in this report (including appendix):
Chemical concentrations are given in metric units, microgram per kilogram (μg/kg), milligram per liter (mg/L), microgram per liter (μg/L), or nanogram per liter (ng/L). Microgram per kilogram is a unit expressing the concentration of a chemical in a solid as weight (microgram) of the chemical per unit weight (kilogram) of soil. One mg/kg is equal to 1,000 μg/kg. Milligram or microgram or nanogram per liter is a unit expressing the concentration of a chemical in solution as weight (milligram or microgram or nanogram) of the chemical per unit volume (liter, L) of water. One mg/L is equivalent to 1,000 μg/L, and 1 μg/L is equivalent to 1,000 ng/L. For concentrations less than 7,000 mg/kg, the numerical value is the same as for concentrations in parts per million; 1 μg/kg is equivalent to 1 part per billion.

Specific conductance of water is expressed in microsiemens per centimeter at 25^o Celsius (μS/cm). This unit is equivalent to micromhos per centimeter at 25^o Celsius (μmho/cm), formerly used by the U.S. Geological Survey.

Nephelometric turbidity unit (ntu) is the unit of measurement for reporting turbidity that is based on use of a standard suspension of Formazin. Turbidity measured in ntu uses nephelometric methods that depend on passing light of a specific wavelength through the sample.

Volumes of water-quality samples are given in liters (L) and milliliters (mL).

Acronyms used in this report:

Acronym	Description
ADCP	Acoustic Doppler Current Profiler
IDEM	Indiana Department of Environmental Management
MDN	Mercury Deposition Network
NADP	National Atmospheric Deposition Program
RPD	Relative Percent Difference
TMDL	Total Maximum Daily Load
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Abstract

Water samples from the Grand Calumet River/Indiana Harbor Canal and Lake Michigan in Lake County, Indiana, were collected and analyzed for mercury. Sampling was done with ultra-clean protocols, and mercury was analyzed by low-level methods during seasons of contrasting weather and streamflow conditions in August 2001 and May 2002.

Total mercury concentrations in all the Grand Calumet River/Indiana Harbor Canal samples exceeded the 1.3 nanogram per liter Indiana water-quality standard for waters within the Great Lakes system. Total mercury concentrations in the Lake Michigan samples did not exceed the Indiana water-quality standard. Total mercury and methylmercury concentrations were larger in more samples collected during the wet-weather streamflow conditions in May 2002 than in samples collected during the dry-weather streamflow conditions in August 2001. The largest total mercury concentrations were in samples collected from the West Branch Grand Calumet River near wetlands and municipal-effluent outfalls (17.2 nanograms per liter) and in samples collected from the Indiana Harbor Canal near the confluence of the East Branch and West Branch Grand Calumet River (16.0 nanograms per liter).

Particulate total mercury was the predominant form of total mercury detected in samples from the Grand Calumet River/Indiana Harbor Canal. Methylmercury concentrations were no more than 1.5 percent of the total mercury concentrations in August 2001 and no more than 6.2 percent in May 2002. Nearly all methylmercury was particulate and was correlated to concentrations of dissolved solids, total organic carbon, and sulfate. The estimated composition of most of the suspended solids in the water samples from the Grand Calumet River/Indiana Harbor Canal was sediment larger than medium clay containing minimal organic carbon and plant matter. Total mercury loads in the Indiana Harbor Canal during the time of water sampling were as large as 703 milligrams per hour in August 2001 and 542 milligrams per hour in May 2002. As much as 21 percent of the instantaneous mercury load in some stream reaches could have come from ground-water discharge.

Data from this study have implications for a Total Maximum Daily Load (TMDL) for mercury in the Grand Calumet River/Indiana Harbor Canal. Comparisons of data from this study with historical data do not show substantial changes in the distribution of mercury in the study area from 1994 through 2002. Treated municipal effluent had larger mercury concentrations than industrial effluent and presents a potential for larger mercury loads that could be controlled to achieve a TMDL, based on concentration. Mercury in ground-water discharge may be difficult to control to achieve a TMDL because of its diffuse and widespread distribution.

Introduction

The Grand Calumet River/Indiana Harbor Canal was first on the Indiana Department of Environmental Management (IDEM) 1998 list of water bodies scheduled for development of a Total Maximum Daily Load (TMDL) for mercury under provisions of the Clean Water Act section 303(d). A TMDL is the largest amount of a specific pollutant (such as mercury) that will not cause in-stream violations of water-quality standards. Mercury was a parameter of concern because of a fish-consumption advisory for the Grand Calumet River/Indiana Harbor Canal (Indiana Department of Environmental Management, 2001). The fish-consumption advisory was based on concentrations of mercury in tissue of fish from the Grand Calumet River/Indiana Harbor Canal that would pose a health risk to humans if consumed. If the mercury concentration in fish tissue results in a fish-consumption advisory, the Indiana water-quality standard[1] of 1.3 nanograms per liter for waters within the Great Lakes system probably was exceeded. This standard protects wildlife that consume fish from health risks caused by mercury ingestion.

A TMDL, if developed, could be used by IDEM to limit mercury in discharges from permitted point sources on the

[1]Indiana Water Pollution Control Board, 2001, Title 327 of the Indiana Administrative Code, Article 2, Rule 1.5, section 8 (327 IAC 2-1.5-8): "Water quality standards applicable to all State Waters within the Great Lakes system, Minimum surface water quality criteria; Table 8–4: Water quality criteria for protection of wildlife; Mercury (including methylmercury)."

Grand Calumet River/Indiana Harbor Canal in an attempt to achieve the Indiana water-quality standard. The mercury TMDL required a base line of mercury data with reporting limits less than the 1.3 ng/L Indiana water-quality standard. The IDEM historical data used reporting limits for mercury in water samples from the Grand Calumet River/Indiana Harbor Canal that were greater than the Indiana standard. Therefore, the historical data were not useful for a TMDL.

To attain the lower reporting limit needed for the mercury TMDL, IDEM requested that the U.S. Geological Survey (USGS) obtain data on the occurrence and distribution of mercury in the Grand Calumet River, the Indiana Harbor Canal, and near-shore Lake Michigan in Lake County, Indiana. The USGS collected samples with ultra-clean protocols and analyzed mercury by low-level methods. To get the base-line mercury data needed, the USGS sampled water in the Grand Calumet River/Indiana Harbor Canal, selected discharges to the Grand Calumet River/Indiana Harbor Canal, and water in Lake Michigan near the water-supply intakes that eventually lead to the permitted discharges.

In addition, the USGS examined the spatial distribution of mercury, the proportions of total mercury and methylmercury in dissolved and particulate forms, seasonal differences in mercury concentrations, and the relation of hydrologic and chemical factors to mercury concentrations. This information could provide a basis for the Grand Calumet River/Indiana Harbor Canal mercury TMDL and for future efforts to develop a mercury TMDL for other water bodies, particularly in northwestern Indiana.

Purpose and Scope

This report presents total mercury and methylmercury concentrations in surface-water samples collected in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan during August 2001 and May 2002. Supplementary water-quality-constituent concentrations and instantaneous streamflow from those time periods also are reported. Relations among concentrations of mercury, water-quality constituents, and streamflow conditions are examined; mercury loads at the time of water sampling are estimated. Factors that may affect a mercury TMDL in the Grand Calumet River/Indiana Harbor Canal are discussed.

Mercury in the Environment

Sources of mercury in surface water include point-source discharges of industrial and municipal wastewater and nonpoint-source atmospheric deposition, stormwater runoff, and ground-water discharge. Atmospheric deposition can contribute mercury directly to lakes and streams. Also, atmospheric deposition to the land can contribute mercury to stormwater runoff and to ground water that enters lakes and streams. Sources of mercury in the atmosphere can be from human activities (coal-fired power plants, waste incinerators, industrial boilers) or can be natural (forest fires, geologic formations, volcanoes). Once in the surface water, mercury can cycle through the sediment, the biota, the water column, and back to the atmosphere (fig. 1).

Methylmercury is produced from inorganic mercury by methylation, a microbial process that is controlled by certain bacteria and chemical variables such as organic matter, sulfate, and oxygen. Sources of mercury emissions to the atmosphere from human activities have been implicated for most of the methylmercury in fish (U.S. Environmental Protection Agency, 1997). A national study of mercury in aquatic ecosystems (Krabbenhoft and others, 1999) indicated larger methylmercury concentrations were related to greater densities of wetlands. Concentrations of methylmercury magnify in the food chain so that higher-level organisms tend to accumulate higher concentrations of methylmercury (fig. 2). Fish living in aquatic ecosystems with extremely low concentrations of inorganic mercury are known to accumulate substantial amounts of methylmercury in their tissue (Krabbenhoft and Rickert, 1995).

Mercury in Indiana's water is a public-health and environmental concern. In Indiana, mercury has been detected in nearly all fish-tissue samples collected since 1983 (Stahl, 1997). Concentrations of mercury in some fish caught in Indiana waters have prompted health officials to issue advisories that warn about human consumption of these fish (Indiana State Department of Health and others, 2000). Mercury—especially in its organic form, methylmercury—can affect the central nervous system of adults and children. A primary exposure to methylmercury for humans is from eating fish caught in rivers and lakes. Because their nervous systems are still in development, infants and young children are predicted to have a greater susceptibility than adults to methylmercury's detrimental effects (National Research Council, 2000). Mercury in Indiana's water is an environmental concern because fish-eating wildlife can suffer damage to the central nervous system from mercury contamination (Krabbenhoft and Wiener, 1999)

Description of the Study Area

The Grand Calumet River/Indiana Harbor Canal in Lake County in northwestern Indiana consists of the East Branch Grand Calumet River, the West Branch Grand Calumet River, and the Indiana Harbor Canal; a part of the West Branch extends into Illinois (fig. 3). As described in Renn (2000), the East Branch Grand Calumet River starts near the Grand Calumet Lagoons, flows west, and discharges to the Indiana Harbor Canal. Streamflow in the West Branch Grand Calumet River divides at a topographic high approximately 1.5 mi west of the confluence with the Indiana Harbor Canal. East of the divide, the West Branch flows toward the Indiana Harbor Canal; west of the divide, the West Branch flows toward Illinois. The Indiana Harbor Canal primarily flows north, discharges into the Indiana Harbor, and then into Lake Michigan.

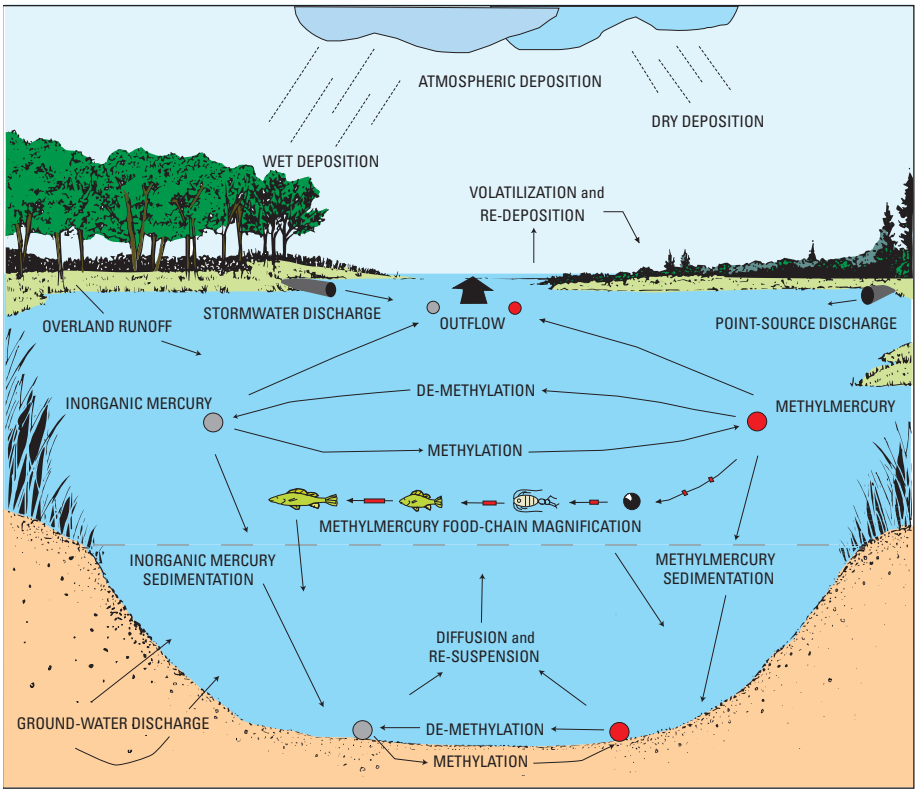


Figure 1. Sources of mercury and mercury cycling in aquatic ecosystems. (Modified from Krabbenhoft and Rickert, 1995.)

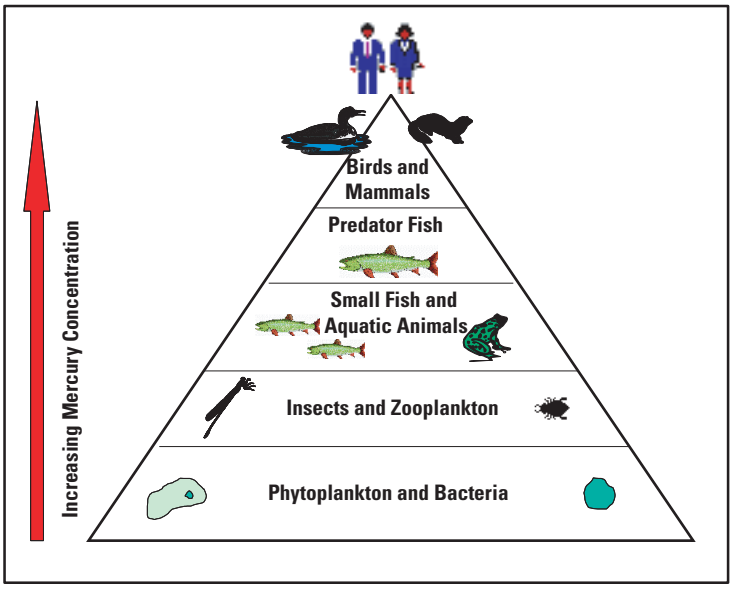


Figure 2. Accumulation and magnification of mercury in the food chain. (Modified from National Wildlife Federation, 2000.)

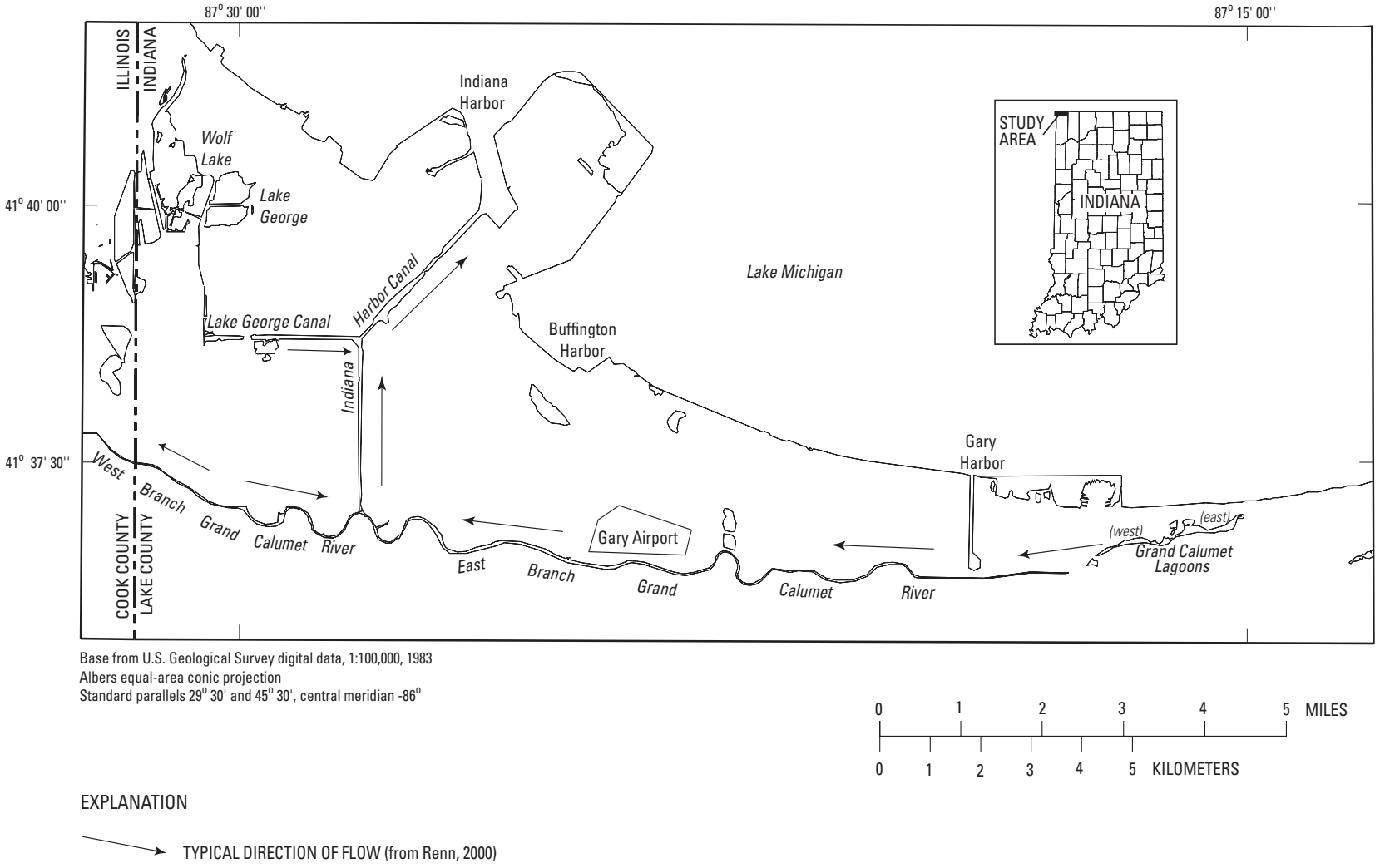


Figure 3. Study area for mercury in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan in Lake County, Indiana, August 2001 and May 2002.

According to Crawford and Wangsness (1987) almost all of the flow in the Grand Calumet River/Indiana Harbor Canal resulted from industrial and municipal discharges, and substantial flow variations have occurred in the East Branch and West Branch Grand Calumet River and in the Indiana Harbor Canal. Also, changes in Lake Michigan water levels temporarily can reverse the direction of flow in the Indiana Harbor Canal and parts of the East Branch and West Branch Grand Calumet River. Parts of the Grand Calumet River/Indiana Harbor Canal have been dredged, channelized, and lined with metal sheet pile. The contribution from surface-water runoff is small. The drainage area of the Grand Calumet River Basin is indeterminate (Stewart and others, 1999) but is estimated to be less than 50 mi^2 (David Cohen, U.S. Geological Survey, 1999, oral commun.).

Fenelon and Watson (1993) report that the study area is underlain by a surficial aquifer that consists primarily of dune, beach, and lacustrine sands ranging from 0 to 65 ft in thickness. Thickest in the east, where the maximum saturated thickness is 45 ft, the aquifer thins to the west and pinches out in lacustrine clay near the Indiana-Illinois state line. The aquifer is underlain by till and lacustrine clay that ranges from 50 to 140 ft in thickness. Model simulations of ground-water flow estimated the aquifer discharges about 15 ft^3/s to sewers, about 10 ft^3/s to the Grand Calumet River/Indiana Harbor Canal, and about 4 ft^3/s to Lake Michigan.

Previous Investigations of Mercury in the Study Area

Historically, concentrations of mercury in water samples analyzed by low-level methods have exceeded the Indiana water-quality standard of 1.3 ng/L total mercury in the Grand Calumet River/Indiana Harbor Canal but generally have not exceeded the standard in Lake Michigan. Previous investigations summarized in this section of the report indicated much of the reported mercury in surface water could be in particulate form, probably arising, in part, from contaminated sediment. Methylmercury was not determined in many of the historical analyses. Overall, mercury was detected in and appeared to be cycling from the atmosphere to ground water, surface water, and sediment; from sediment into surface water; and from surface water and sediment into fish.

Mercury in Surface Water

Limited historical data were available for mercury in Lake Michigan and the Grand Calumet River/Indiana Harbor Canal. Two data sets were summarized for this report—the Lake Michigan Mass Balance Study in 1994 and 1995 sponsored by the U.S. Environmental Protection Agency (USEPA) and USGS sampling in July 1999.

Mercury in Lake Michigan

As part of the Lake Michigan Mass Balance Study, water-column samples from offshore and open water Lake Michigan were collected in 1994 and 1995 (Mason and Sullivan, 1997). Samples were collected and analyzed with methods comparable to low-level methods. From 132 samples, the mean concentration of total mercury was 0.32 ng/L; 36 percent of the total mercury was in particulate form. From 26 samples, the mean concentration of methylmercury was 0.013 ng/L; 25 percent of the methylmercury was in particulate form. Mercury concentrations were not stratified with depth, nor was there a north-south trend in concentrations. A budget for sources and sinks of mercury in Lake Michigan estimated that atmospheric deposition accounted for about 80 percent of the total input; about 17 percent of the total input was from tributaries (Mason and Sullivan, 1997).

Mercury in the Grand Calumet River/ Indiana Harbor Canal

As part of the Lake Michigan Mass Balance Study, 11 selected tributaries were sampled, including the Indiana Harbor Canal (Hurley and others, 1996). The study included 10 USEPA-designated Areas of Concern and 1 background site. Samples were collected with ultra-clean protocols and analyzed by low-level methods. Two samples were collected at the Indiana Harbor Canal—one during summer base flow and one after a late summer/early fall storm. The total mercury concentration during base flow was 13.5 ng/L, of which 12.2 ng/L (90 percent) was particulate mercury. The total mercury concentration after the summer/fall storm was 7.75 ng/L, of which 7.25 ng/L (94 percent) was particulate mercury. In the two samples, the suspended particulate matter was 7 and 8 mg/L and the dissolved organic carbon was 3.25 and 3.50 mg/L. Among the trace metals detected (mercury, lead, zinc, cadmium, and copper), most were in the particulate form and mercury was the highest percentage particulate.The highest percentage for particulate metals in all the tributaries sampled was reported for the Indiana Harbor Canal. Contaminated sediments were implicated as a likely source of the particulate metals, including mercury (Hurley and others, 1996).

During July 1999, the USGS collected unfiltered samples for total mercury analysis by the low-level method—four from the Indiana Harbor Canal and six from the Grand Calumet River. The samples were collected without ultra-clean protocols, but quality-control blanks did not indicate laboratory- or sampling-artifact mercury (Richard Duwelius, U.S. Geological Survey, 2001, oral commun.). Mercury concentrations in the Indiana Harbor Canal ranged from 2.1 to 5.2 ng/L and from 1.5 to 19 ng/L in the Grand Calumet River (Stewart and others, 2001).

Mercury in Fish, Sediment, Atmospheric Deposition, and Ground Water

Historical mercury data were summarized in this report for samples of a common and widespread fish species and for samples of streambed-sediment collected by IDEM in the study area. Data regarding mercury in atmospheric wet deposition were summarized for 2001 and 2002 from a monitoring station near the study area and compared with statewide, regional, and national atmospheric-deposition data. Mercury data from ground-water samples in the study area were summarized, including estimated loads of mercury in ground water discharged to the Grand Calumet River/Indiana Harbor Canal.

Mercury in Fish

The 2000 Indiana Fish Consumption Advisory (Indiana State Department of Health and others, 2000) listed a "do not eat because of high levels of contamination" advisory for fish from the Grand Calumet River/Indiana Harbor Canal. Mercury is the contaminant listed in the advisory for 12 size classes of seven species of fish in the Lake County tributaries of Lake Michigan, resulting in a "do not eat" or "limit consumption" advisory.

A variety of fish species have been observed in the Grand Calumet River/Indiana Harbor Canal (Newhouse and others, 1997); carp is one of the most common and widespread species. IDEM collected 9 to 22 individual carp at five locations in the Grand Calumet River/Indiana Harbor Canal, 1980 through 1996, and obtained mercury analysis of whole carp and carp fillets (James Stahl, Indiana Department of Environmental Management, 2001, written commun.). Maximum concentrations of mercury for 66 samples of carp tissue from mixed-size classes and preparations (whole or fillet) at the five locations ranged from 142 to 267 µg/kg. Some of the maximum concentrations of mercury in carp in the Grand Calumet River/Indiana Harbor Canal approach the USEPA water-quality criterion for methylmercury, 300 µg/kg in fish tissue (U.S. Environmental Protection Agency, 2001a). Although reported as total mercury, nearly all of the mercury in fish tissue is presumed to be methylmercury, the form of mercury that bioaccumulates and biomagnifies in the food chain (U.S. Environmental Protection Agency, 1997 and 2001a).

Mercury in Streambed Sediment

Streambed sediments can cycle mercury into the aquatic ecosystem for decades or longer (U.S. Environmental Protection Agency, 1997 and 2001a). Eight streambed-sediment composite samples collected by IDEM in 1994 and 1996 from six locations in the Grand Calumet River/Indiana Harbor Canal ranged from 20 to 230 µg/kg mercury on a dry-weight basis (James Stahl, Indiana Department of Environmental Management, 2000, written commun.). Among all IDEM streambed-sediment data, the mean mercury concentration for Lake County was 300 µg/kg, compared with a statewide mean of 58 µg/kg and statewide 95th percentile of 341 µg/kg (Wente, 1997).

Mercury in Atmospheric Deposition

Atmospheric deposition, primarily wet deposition, can be a substantial source of mercury input to aquatic ecosystems (U.S. Environmental Protection Agency, 1997 and 2001a). Mason and Sullivan (1997) attributed atmospheric deposition as 80 percent of the total mercury input in the estimated total mercury budget for Lake Michigan.

In 2001 and 2002, wet-deposition samples were collected near the study area at the Indiana Dunes National Lakeshore, a monitoring site in the National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN). The NADP is a cooperative research support program that collectively operates wet-deposition monitoring stations in North America and has sponsored the MDN since 1996. In 2002, the MDN had more than 70 active monitoring stations, including 4 in Indiana (fig. 4).

Data for mercury concentrations and mercury wet-deposition rates at the Indiana Dunes National Lakeshore in 2001 and 2002 are summarized in table 1; concentrations and rates for the Indiana and North American MDN stations are included for comparison. (If data from the Indiana Dunes National Lakeshore monitoring station are representative of the Grand Calumet River Basin drainage area, the atmospheric wet deposition of mercury in the basin in 2001 and 2002 was approximately 1,330 grams per year[2].)

Mercury in Ground Water

Duwelius and others (1996) reported concentrations of mercury in the ground water of the Calumet region in Indiana and Illinois in June 1993; this study area includes the Grand Calumet River/Indiana Harbor Canal. Ultra-clean protocols were not used for mercury-sample collection and low-level methods were not used for mercury analysis. Mercury was detected at concentrations larger than 0.1 or 0.2 µg/L in 53 percent (69 of the 129) of the ground-water samples collected in the study area. Of the samples in which mercury was detected, 67 percent (46 of 69) were from the surficial aquifer. The maximum mercury concentration was 1.1 µg/L; the USEPA drinking-water standard (Maximum Contaminant Level) for mercury is 2 µg/L. Some of the estimated mercury concentrations between 0.1 to 0.2 µg/L could have been artifacts because mercury was detected in the laboratory blanks;

[2]The estimate for atmospheric wet deposition of mercury was computed with a 129.5-km^2 (50-mi^2) drainage area multiplied by the sum of the total annual mercury wet deposition of mercury at the Indiana Dunes National Lakeshore monitoring station (20,640 ng/m^2).

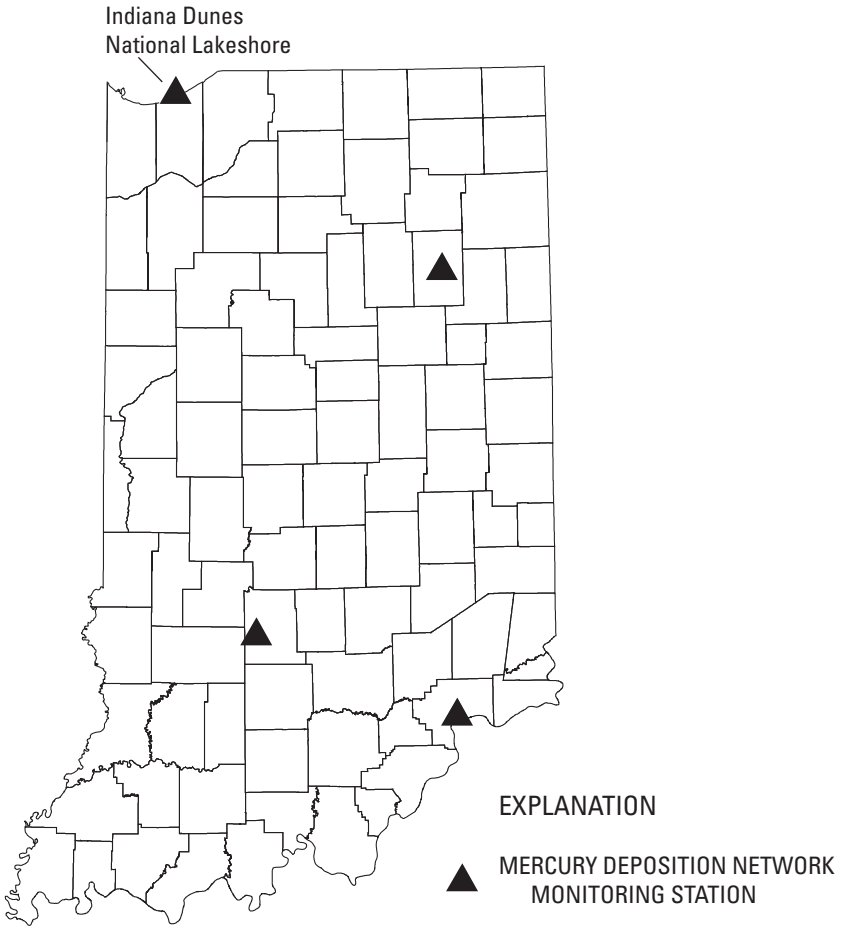


Figure 4. Locations of Indiana monitoring stations for mercury in wet deposition during 2001 and 2002.

Table 1. Mercury concentrations and mercury wet-deposition rates for National Atmospheric Deposition Program Mercury Deposition Network monitoring stations in Indiana and North America.

[ng/L, nanogram per liter; ng/m^2, nanogram per square meter]

Monitoring station(s)	Time period	Annual mean concentration of total mercury (ng/L)	Mean weekly wet deposition of total mercury (ng/m^2)	Annual total wet deposition of total mercury (ng/m^2)
Indiana Dunes National Lakeshore[a]	2001	12.0	226	11,050
Indiana Dunes National Lakeshore[a]	2002	13.0	213	9,590
Four monitoring stations in Indiana[a]	2001	11.6	225	11,900
Four monitoring stations in Indiana[a]	2002	12.8	253	11,500
Mercury Deposition Network stations in North America[b]	1996 through1999	10.0	200	10,000

[a]Data from U.S. Geological Survey (2003).

[b]Data from National Atmospheric Deposition Program (2000) and Sweet and Prestbo (1999).

more confidence was reported for concentrations larger than 1 µg/L. Mercury, ranging from 0.14 to 1.1 µg/L, was detected in 75 percent of the samples from 12 wells screened in the surficial aquifer near the Gary Airport; the median concentration was 0.14 µg/L, which is equivalent to 140 ng/L.

Willoughby and Siddeeq (2001) calculated chemical loads from ground water to the Grand Calumet River/Indiana Harbor Canal with historical ground-water-quality data and two different daily ground-water fluxes. The fluxes were based on two different horizontal hydraulic-conductivity values for the surficial aquifer (Fenelon and Watson, 1993). For mercury, estimated maximum loads from ground water ranged from 8.3 to 83 mg/hr for selected reaches of the river.

Methods

This section describes the study design and selection of sampling locations for mercury in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan. The sampling procedures and equipment are discussed. The analytical methods and quality assurance for field determinations and laboratory analysis are explained. The technique for instantaneous streamflow measurement is described.

Study Design

Previous investigations indicated much of the mercury in Lake Michigan tributaries was particulate (Hurley and others, 1996); it is likely then that suspended sediment in these tributaries included particulate mercury. From 1996 through 1998, the USGS analyzed 1,856 suspended-sediment samples and streamflow values from the Indiana Harbor Canal (Renn, 2000). Unlike in other streams in Indiana, no statistical relation between streamflow and suspended sediment was shown in the Indiana Harbor Canal; however, suspended-sediment concentrations were seasonally highest in spring and lowest in late summer. Therefore, mercury sampling was done in summer 2001 and spring 2002 to investigate any influence of suspended sediment on particulate mercury. Dry summer weather and wet spring weather offered a contrast in streamflow with and without storm runoff. Also, summer and spring provided contrast in air and water temperature, affecting microbiological activity for methylmercury production.

Mercury can be dissolved in water and bound to suspended particulate matter in water (U.S. Environmental Protection Agency, 1997). In this study, dissolved total mercury and dissolved methylmercury were analyzed in filtered water samples. Particulate total mercury and particulate methylmercury were analyzed from the filters. To evaluate potential transport of mercury, water samples were analyzed for organic carbon, major ions and nutrients, and dissolved solids. To evaluate potential transport of particulate mercury, the concentrations of suspended sediment, suspended fine particulates, and plant pigments (chlorophyll-a and pheophytin-a) were determined from residue on filters.

The capability for load estimates was included in the study design. Instantaneous streamflow measurements were made at flowing-water sampling locations so that hydrologic conditions could be compared. Sampling was done in a synoptic, short-duration time period so that hydrologic conditions would be similar. To collect water-supply and effluent samples at their facilities during the USGS sampling, IDEM coordinated with one municipality and two industries that had permitted outfalls in the study area.

Sampling Locations

Previous investigations and a conceptual understanding of mercury sources and mercury transport in the study area were used to select sampling locations. Among the factors considered were

- Water withdrawn from Lake Michigan is discharged to the Grand Calumet River/Indiana Harbor Canal in noncontact cooling water and treated effluent from industries and in treated effluent from municipal outfalls.
- Ground-water discharges through streambed sediments along much of the Grand Calumet River and parts of the Indiana Harbor Canal during typical flow conditions.
- Wetland density is greatest in two areas along the East Branch and West Branch Grand Calumet River where potentially larger concentrations of methylmercury could be found.

A total of 17 sampling locations on the Grand Calumet River/Indiana Harbor Canal and Lake Michigan (fig. 5) were selected and are described in downstream order in table 2. Of the 14 surface-water sampling locations, 8 locations on the Grand Calumet River/Indiana Harbor Canal correspond with mercury sampling by the USGS in 1999; 10 locations on the Grand Calumet River/Indiana Harbor Canal include 8 stream reaches designated in a previous investigation by the USGS to estimate chemical loads from ground water to the Grand Calumet River/Indiana Harbor Canal (Willoughby and Siddeeq, 2001). Five locations on the Grand Calumet River (M19, M14, M13, M12, and M9) were near wetlands. Three locations on Lake Michigan (IH1, LM1, and LM2) were near industrial water-supply intakes. IDEM requested the USGS sample treated effluent at three locations—an industrial outfall on the Indiana Harbor Canal (IO1) and two municipal outfalls on the West Branch Grand Calumet River (MO1 and MO2).

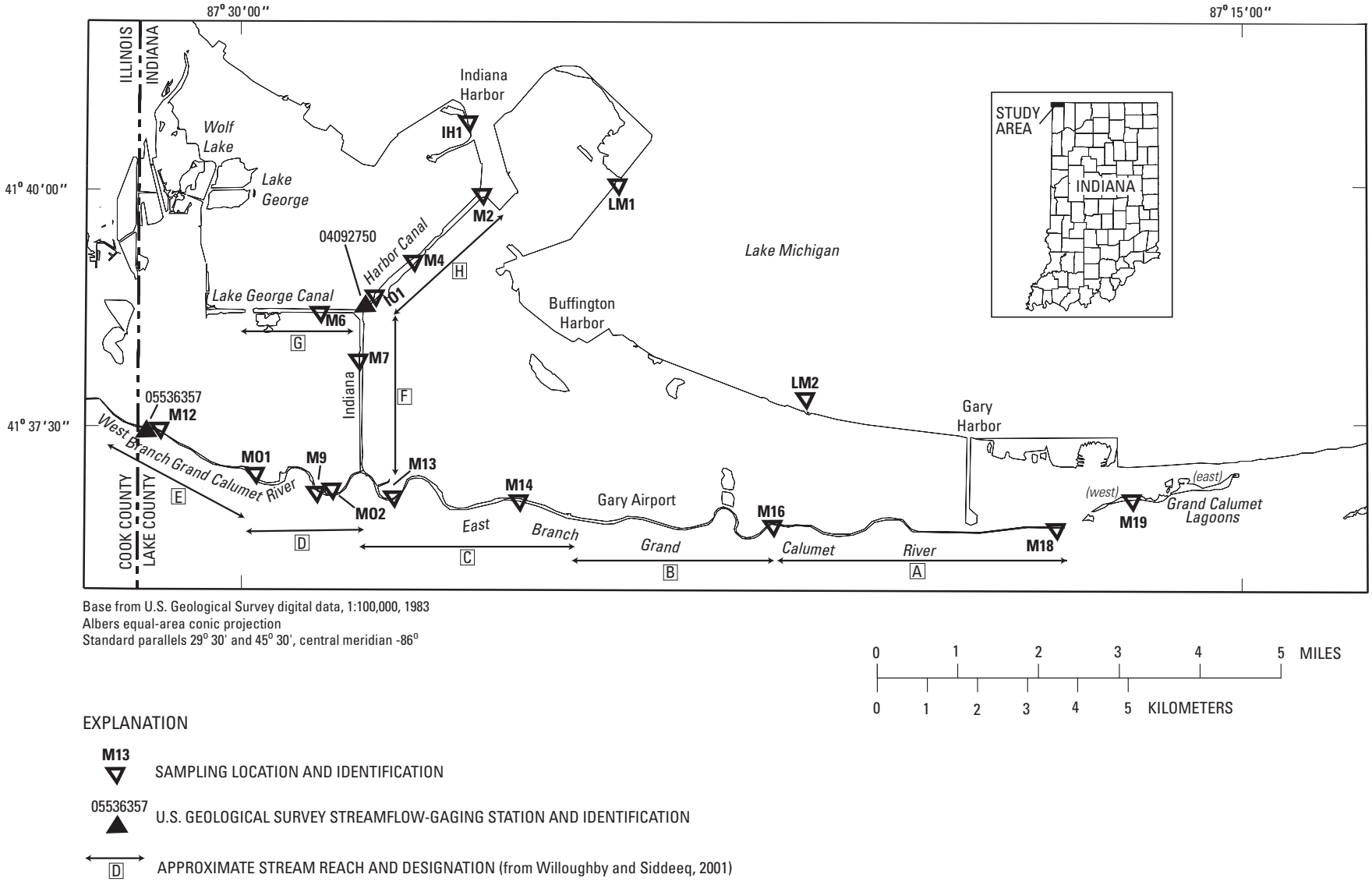


Figure 5. Sampling locations for mercury in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan in Lake County, Indiana, August 2001 and May 2002.

Table 2. Locations for mercury sampling in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001 and May 2002.

[Locations listed in downstream order; reach designations A through H from Willoughby and Siddeeq (2001)—see figure 5; ID, identification; M, location in main channel of Grand Calumet River/Indiana Harbor Canal; MO, location at municipal outfall; IO, location at industrial outfall; IH, location in Indiana Harbor; LM, location in Lake Michigan]

Location ID	Location name	Location purpose
M19[a]	Grand Calumet Lagoons, west	Upstream from all outfalls; wetland area; minimal flow.
M18[a]	East Branch Grand Calumet River downstream from the Grand Calumet Lagoons, west	Headwaters of East Branch Grand Calumet River; upstream from all outfalls; upstream end of Reach A; minimal flow.
M16	East Branch Grand Calumet River at Bridge St.	Downstream end of reach A; downstream from industrial cooling-water and treated process-water outfalls.
M14	East Branch Grand Calumet River at Cline Ave.	Near the downstream end of reach B; downstream from municipal outfall; wetland area.
M13[a]	East Branch Grand Calumet River at Kennedy Ave.	Near the downstream end of reach C; wetland area.
M12[a]	West Branch Grand Calumet River at Hohman Ave.	Near the downstream end of reach E; upstream from municipal outfalls; wetland area.
MO1	West Branch Grand Calumet River municipal outfall 1	Assessment of municipal effluent.
M9[a]	West Branch Grand Calumet River at Indianapolis Blvd.	Near the downstream end of reach D; downstream from municipal outfalls; wetland area.
MO2	West Branch Grand Calumet River municipal outfall 2	Assessment of municipal effluent.
M7[a]	Indiana Harbor Canal at Columbus Dr.	Near the downstream end of reach F; integrates East Branch and West Branch of Grand Calumet River.
M6[a]	Indiana Harbor Canal at Lake George Canal	Near the downstream end of reach G.
IO1	Indiana Harbor Canal industrial outfall	Assessment of industrial effluent.
M4	Indiana Harbor Canal at Dickey Rd.	Upstream from industrial outfalls; integrates Lake George Canal.
M2[a]	Indiana Harbor Canal at mouth of Indiana Harbor	Downstream end of reach H; downstream from outfalls on Indiana Harbor Canal; confluence of Indiana Harbor Canal with Lake Michigan.
IH1	Indiana Harbor near industrial intake	Assessment of water supply for industrial discharge.
LM1	Lake Michigan near industrial intake 1	Assessment of water supply for industrial discharge.
LM2	Lake Michigan near industrial intake 2	Assessment of water supply for industrial discharge.

[a]Mercury sampling location in July 1999 (Stewart and others, 2001).

Sampling Procedures

This section describes the ultra-clean protocols for collection of water and effluent samples for low-level mercury analysis, along with the specific equipment, supplies, and watercraft that were used. Three types of sampling approaches are explained. Methods for mercury analysis and quality control are identified.

Equipment and Supplies

Water samples were obtained with a peristaltic-pump apparatus (fig. 6). A Teflon weight with intake ports was lowered with a Kevlar hand line to the desired sampling depths. The weight was connected to an optimal length of small-diameter Teflon tubing inserted in a short piece of silicone flex tubing at the pump head. When used, a Teflon filter holder with a preloaded glass-fiber particulate filter was connected to the flex tubing. Mercury-sampling supplies were prepared at the USGS Mercury Research Laboratory in Wisconsin. Following the ultra-clean protocols, the weights, hand lines, and single-use sets of sampling supplies[3] were decontaminated in a Class 100 clean room environment, double bagged, and placed in shipping containers (Olson and others, 2000). A portable glove box was used for sample preservation in the field. The mercury-sampling equipment and supplies used were consistent with USEPA Method 1669 (U.S. Environmental Protection Agency, 1996).

An isokinetic, depth-integrating sampler was used for collection of suspended-sediment samples, consistent with the USGS National Field Manual (Wilde and Radtke, 1998). A portable, multi-parameter electronic meter was used to measure water-quality characteristics (pH, specific conductance, dissolved oxygen concentration, and water temperature). A portable turbidimeter (Hach model 2100P) was used to measure turbidity. A portable pH meter with temperature compensation and a digital titrator were used for alkalinity determinations.

[3]Teflon tubing, Teflon bottles, silicone flex tubing and Teflon filter holders.

Watercraft and Vehicles

Sample collection on the Grand Calumet River/Indiana Harbor Canal, Grand Calumet Lagoons (west), and Indiana Harbor was done from an inflatable, rubberized boat with wooden floors and transom (fig. 7). The boat was held stationary by a cable tagline stretched across the stream channel and a resin-coated anchor. All anchor lines were nylon. Sample collection on Lake Michigan was done from the stern of an anchored, fiberglass ship. A mobile water-quality laboratory was used to process samples and to complete alkalinity titrations. Watercraft and vehicle procedures were consistent with USEPA Method 1669.

Sample Collection

Water samples for total mercury and methylmercury analysis were collected by ultra-clean trace-metals protocols consistent with the USEPA (1996), Wilde and Radtke (1998), and Horowitz and others (1994). Ultra-clean protocols are designed to avoid the unintentional introduction of low levels of trace metals, such as mercury, into a sample. Two USGS personnel collected samples. To protect sample integrity, sampling personnel wore disposable coveralls, hats, face shields, and powder-free disposable gloves (fig. 7).

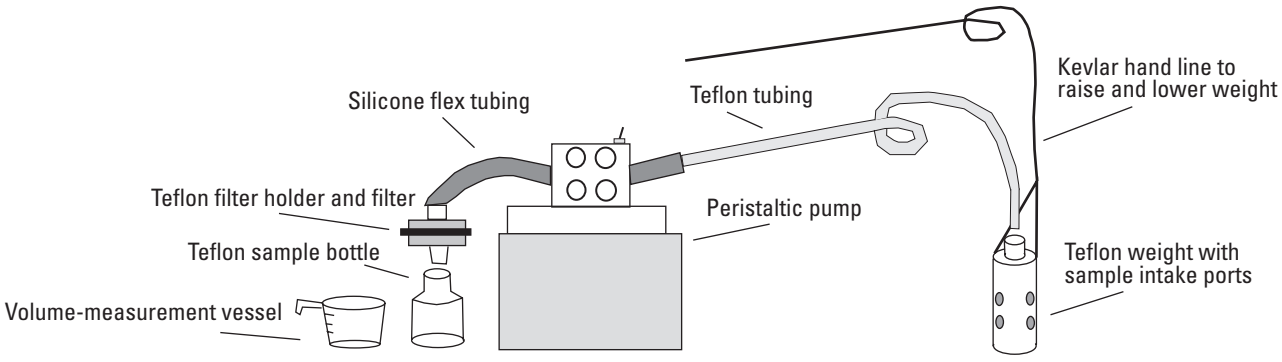


Figure 6. Peristaltic-pump apparatus for mercury sampling, August 2001 and May 2002, in Lake County, Indiana.

Figure 7. Watercraft and U.S. Geological Survey personnel during mercury sampling, Lake County, Indiana, August 2001.

Three types of sampling approaches were used to collect a representative sample for each location, following procedures in Wilde and Radtke (1998).

1. At locations in the Grand Calumet River/Indiana Harbor Canal, depth-integrated composite samples were collected at the center of three equal-width sections. Stream width was measured with an incremented tagline, and stream depth was determined at the center of each section with a weighted measuring tape. At each sampling interval, the pump intake was raised and lowered at a constant rate until the desired sample volume was obtained.
2. At locations in the Grand Calumet Lagoons (west), Indiana Harbor, and Lake Michigan, samples were composited with equal portions from the center of three equal-length sections of a single vertical. Length of the water column was determined at each vertical with a weighted measuring tape.
3. At locations of effluent outfalls, point samples were collected in the center of flow.

The mercury-sampling supplies for a location were sorted into plastic boxes inside a larger supply box to isolate them from airborne mercury. Repeated glove changes were made so that sample bottles were handled only with new gloves. Teflon bottles provided by the USGS Mercury Research Laboratory were pre-cleaned, pre-charged with high-purity 1-percent hydrochloric acid, and quality assured as described in the laboratory's quality-assurance plan. Bottles were shaken, and the acid was discarded before filling. For filtered samples, at least 1.5 L of sample water were pumped through a 0.45-µm pore-size filter—one filter for particulate total mercury analysis and another filter for particulate methylmercury analysis. Water samples for mercury and methylmercury analysis were kept in the dark immediately after collection until they were preserved with high-purity hydrochloric acid under controlled conditions in a glove box in the mobile laboratory. Filters for particulate mercury and methylmercury analysis were frozen on dry ice. Table 3 lists containers, treatment, and preservation for mercury and supplementary constituents.

Water-Quality Analysis

Mercury and organic carbon analyses were done by the USGS Mercury Research Laboratory. Analysis for total mercury was by "oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry" (Olson and DeWild, 1997a), equivalent to USEPA Method 1631 (U.S. Environmental Protection Agency, 1999). Analysis for methylmercury was by "aqueous-

Table 3. Constituents, containers, treatment, and preservation for sampling during August 2001 and May 2002 in Lake County, Indiana.

[mL, milliliter; HCl, high-purity hydrochloric acid added to a concentration of 1 percent (%) by volume; µm, micrometer; °C, degree Celsius; < , less than; L, liter;]

Constituent	Container	Volume	Treatment	Preservation
Total mercury, unfiltered	Teflon, pre-cleaned[a]	500 mL	None	HCl to 1%; keep in darkness.
Methylmercury, unfiltered	Teflon, pre-cleaned[a]	250 mL	None	HCl to 1%; keep in darkness.
Dissolved total mercury	Teflon, pre-cleaned[a]	500 mL	.45-µm quartz-fiber filter	HCl to 1%; keep in darkness.
Dissolved methylmercury	Teflon, pre-cleaned[a]	250 mL	.45-µm quartz-fiber filter	HCl to 1%; keep in darkness.
Particulate total mercury	.45-µm quartz-fiber filter	None	1.5-L sample per filter	Freeze with dry ice immediately.
Particulate methylmercury	.45-µm quartz-fiber filter	None	1.5-L sample per filter	Freeze with dry ice immediately.
Total organic carbon	Glass vial, new	40 mL	None	Chill to 4°C.
Dissolved organic carbon	Glass vial, new	40 mL	.45-µm capsule filter	Chill to 4°C.
Dissolved solids	Polyethylene, new	250 mL	.45-µm capsule filter	Chill to 4°C.
Dissolved chloride, sulfate, phosphate, and fluoride	Polyethylene, new	250 mL	.45-µm capsule filter	Chill to 4°C.
Dissolved calcium, magnesium, potassium, sodium, iron, silica, and manganese	Polyethylene, new	250 mL	.45-µm capsule filter	1 Molar nitric acid to pH < 2; chill to 4°C.
Chlorophyll-a, pheophytin-a phytoplankton biomass	Three .7-µm glass-fiber filters	None	125-mL sample per filter	Place in petri dish; wrap in foil; freeze with dry ice immediately.
Suspended sediment	Glass, tared	1 L	None	None.

[a]Sample containers were 25-percent filled with high-purity 1-percent hydrochloric acid that was discarded before samples were collected.

phase ethylation and gas chromatography separation with cold vapor atomic fluorescence detection" (DeWild and others, 2002) equivalent to USEPA Method 1630 (U.S. Environmental Protection Agency, 1998). All total mercury and methylmercury determinations were made on duplicate aliquots from each sample, and concentrations in this report are the averages of the duplicate-aliquot analyses. Detection limits for total mercury and methylmercury in groups of samples were determined by the laboratory through analysis of calibration standards and blanks. Detection limits are listed with the analytical results in the appendixes (table 1–1, table 2–1).

Analysis for most supplementary constituents (dissolved solids, dissolved major ions, nutrients, and plant pigments) was done by the USGS National Water Quality Laboratory in Colorado. Analysis for suspended sediment was done by the USGS Northeastern Region Sediment Laboratory in Kentucky. Incremental titrations for calcium-carbonate alkalinity were done in the mobile laboratory. Dissolved major ions and nutrients were analyzed in approximately half of the water samples selected to be representative of the study area. Supplementary constituents and analytical methods are listed in table 4.

Quality Control

Approximately one third of all samples analyzed for mercury were quality-control field-blank samples used to determine if mercury was introduced unintentionally into samples. Field-blank water for mercury analysis was provided by the USGS Mercury Research Laboratory. Parts of the sampling apparatus were isolated for preparation of field-blank samples, including the tubing, filter holder, sample bottle, and blank-water container. Blanks for the tubing and filter holder were pumped from the blank-water container with the peristaltic pump. The field blank for the sample bottle was poured from the blank-water container. Field-blank samples were preserved, handled, and transported with the other water samples. Samples of the preservative and blank water were obtained at the Mercury Research

Table 4. Analytical methods for supplementary constituents in water samples during August 2001 and May 2002 in Lake County, Indiana.

[mg/L, milligram per liter; $CaCO_3$, calcium carbonate]

Constituent	Analytical method	Published reference	Reporting limit (mg/L)
Chloride	Ion chromatography	Fishman and Friedman, 1989	0.08
Fluoride	Ion-selective electrode	Fishman and Friedman, 1989	.16
Sulfate	Ion chromatography	Fishman and Friedman, 1989	.11
Phosphate, ortho	Colorimetry	Fishman, 1993	.018
Alkalinity, $CaCO_3$	Incremental titration	Wilde and Radtke, 1998	1.0
Calcium	Inductively coupled plasma spectrometry	Fishman, 1993	.011
Magnesium	Inductively coupled plasma spectrometry	Fishman, 1993	.008
Sodium	Inductively coupled plasma spectrometry	Fishman, 1993	.06
Potassium	Atomic absorption flame spectrometry	Fishman and Friedman, 1989	.09
Silica	Colorimetry	Fishman and Friedman, 1989	.48
Iron	Inductively coupled plasma spectrometry	Fishman, 1993	.01
Manganese	Inductively coupled plasma spectrometry	Fishman, 1993	.0032
Dissolved solids	Gravimetric	Fishman and Friedman, 1989	10
Organic carbon	Heat-assisted persulfate oxidation	Olson and DeWild, 1997b	.1
Chlorophyll-a	Fluorometry, chromatography	Britton and Greeson, 1989	.0001
Pheophytin-a	Fluorometry, chromatography	Britton and Greeson, 1989	.0001
Seston[a]	Gravimetric	Fishman and Friedman, 1989	.1
Suspended sediment	Gravimetric	Guy, 1969	1.0

[a]Ash-free dry weight.

Laboratory from what remained in the containers after use in the field. The laboratory also provided analysis of blank water not transported to the field.

Laboratory quality-control samples were prepared and analyzed in a manner consistent with USEPA Method 1631 (U.S. Environmental Protection Agency, 1999). Field and laboratory quality-control data were evaluated according to the USEPA Method 1631 and Guidance for Implementation of Method 1631 (U.S. Environmental Protection Agency, 2001b).

Field-collected, laboratory-blind, sequential duplicate samples were collected to investigate the natural variability of constituent concentrations in flowing and still water. The duplicate sample was collected immediately following the first sample at each of the three horizontal or vertical sections.

Streamflow

Instantaneous streamflow was measured, where flow was sufficient, while water samples were collected at sampling locations on the Grand Calumet River/Indiana Harbor Canal. Acoustic Doppler current profiler (ADCP) methods were used in August 2001 at sampling locations M16, M14, M13, and M6 and in May 2002 at sampling locations M16 and M13. A 1200-kilohertz ADCP was deployed from a tethered platform, and data were collected on a portable field computer with radio telemetry. USGS protocols for ADCP measurements (Lipscomb, 1995) were followed; streamflow data were processed, checked, and archived. Standard USGS methods for measurement of streamflow (Rantz and others, 1982) were used in August 2001 at sampling location M9 and in May 2002 at

sampling locations M14 and M9. A Price AA mechanical current meter and 30-lb sounding weight suspended from a bridge crane and connected to an electronic discharge-measurement interface collected and processed the streamflow data. For the 60-minute periods of water sampling at locations M7, M4, and M2, streamflow was computed as the mean of four 15-minute-interval values from USGS streamflow-gaging station 04092750. For sampling location M12, the nearest hourly instantaneous streamflow value from USGS streamflow-gaging station 05536357 on the West Branch Grand Calumet River was used.

Mercury in the Grand Calumet River/ Indiana Harbor Canal and Lake Michigan

This section describes the results from August 2001 and May 2002 for total mercury and methylmercury in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, including the quality-control samples. A discussion of the relation of streamflow, sampling locations, and water-quality constituents to mercury concentrations is presented. Estimated loads of total mercury at the time of sampling are presented, and mercury concentrations in effluent are summarized. Implications for a mercury TMDL are discussed.

Total Mercury and Methylmercury

Laboratory determinations of "total mercury" for this study included inorganic mercury and methylmercury, although methylmercury also was determined separately. In this report, total mercury or methylmercury determinations from a filtered sample are termed "dissolved total mercury" or "dissolved methylmercury." When the filters were processed at the laboratory and analyzed for total mercury or methylmercury, determinations from a filter are particulate-bound mercury, termed "particulate total mercury" or "particulate methylmercury." The sum of dissolved and particulate total mercury concentrations is termed "combined total mercury." The sum of dissolved and particulate methylmercury is termed "combined methylmercury." When dissolved methylmercury was not detected, the combined methylmercury is assumed to be equivalent to the particulate methylmercury. Total mercury or methylmercury determinations from an unfiltered sample are termed "unfiltered total mercury" or "unfiltered methylmercury."

Samples collected during August 2001 from the Grand Calumet River/Indiana Harbor Canal and Lake Michigan were analyzed for dissolved and particulate total mercury and dissolved and particulate methylmercury; effluent samples were analyzed for unfiltered total mercury. Samples collected during May 2002 from the Grand Calumet River/Indiana Harbor Canal and Lake Michigan were analyzed for dissolved and particulate total mercury; effluent samples were analyzed for unfiltered total mercury. All of the 2002 samples were analyzed for unfiltered methylmercury. Because dissolved methylmercury was not detected in 13 of the 14 samples for 2001 (appendix: table 1–1), 5 samples were analyzed for dissolved and particulate methylmercury in 2002.

Mercury concentrations listed in the appendixes and discussed in this section are mean values from analysis of duplicate aliquots from each sample bottle. For sampling locations with field-duplicate samples, the largest concentration is used to report the maximum range of concentrations and to estimate the maximum instantaneous mercury load; these values may be more relevant to application of the data in a TMDL. Both concentrations from field-duplicate samples are used in the discussion of natural variability in the section, Factors Affecting Mercury Concentrations and Mercury Transport. Combined total mercury and combined methylmercury concentrations are used in discussions of samples collected during 2001 and 2002. For sampling locations from 2002 without combined methylmercury concentrations, the unfiltered methylmercury concentration was substituted.

Mercury in Environmental Samples

Ranges of combined total mercury and methylmercury concentrations in water samples from groups of sampling locations are presented in table 5. The largest combined total mercury concentrations during August 2001 (appendix: table 1–1) were in the Indiana Harbor Canal near the confluence of the East Branch and West Branch Grand Calumet River (M7, 16.0 ng/L) and in the West Branch Grand Calumet River near wetlands and municipal-effluent outfalls (M9, 15.9 ng/L). The largest combined total mercury concentration during May 2002 (appendix: table 2–1) was in the West Branch Grand Calumet River near wetlands (M12, 17.2 ng/L). The largest combined methylmercury concentrations were in the West Branch Grand Calumet River during August 2001 (M12, 0.091 ng/L; M9, 0.050 ng/L) and during May 2002 (M12, 0.181 ng/L; M9, 0.147 ng/L). Combined methylmercury as a percentage of the combined total mercury concentration was as large as 1.5 percent during August 2001 and 6.2 percent during May 2002 (table 6).

During August 2001 (fig. 8), the combined total mercury concentrations in all samples from the Grand Calumet River/ Indiana Harbor Canal exceeded the Indiana water-quality standard of 1.3 ng/L for waters in the Great Lakes system; the mean concentration was 5.89 ng/L. Combined total mercury concentrations at three locations in Lake Michigan (maximum 0.34 ng/L) were less than the standard. The maximum concentration in the West Branch Grand Calumet River (15.9 ng/L at M9) was larger than the maximum concentration in the East Branch Grand Calumet River (5.2 ng/L at M16) and similar

Table 5. Ranges of combined total mercury and methylmercury concentrations in water samples from groups of sampling locations on the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001 and May 2002.

[Concentrations of mercury in nanogram per liter (ng/L); IDs, identifications; < , less than reporting limit listed]

Group of sampling locations and location IDs	Ranges of combined total mercury concentrations[a]		Ranges of combined methylmercury concentrations[b]	
	August 2001	May 2002	August 2001	May 2002
East Branch Grand Calumet River (M18, M16, M14, M13)	2.56 - 5.25	1.63 - 7.25	0.008 - 0.013	<0.002 - 0.117
West Branch Grand Calumet River (M12, M9)	6.30 - 15.9	5.48 - 17.2	.050 - .091	.147 - .181
Indiana Harbor Canal (M7, M6, M4, M2)	2.28 - 16.0	4.38 - 6.87	.010 - .024	<.002 - .068
Grand Calumet Lagoons, west (M19)	3.17	3.21	.030	.046
Lake Michigan near water intakes (IH1, LM1, LM2)	.18 - .34	1.31 - 3.06	.001 - .004	<.002 - .004

[a]Combined total mercury is the sum of dissolved and particulate concentrations.

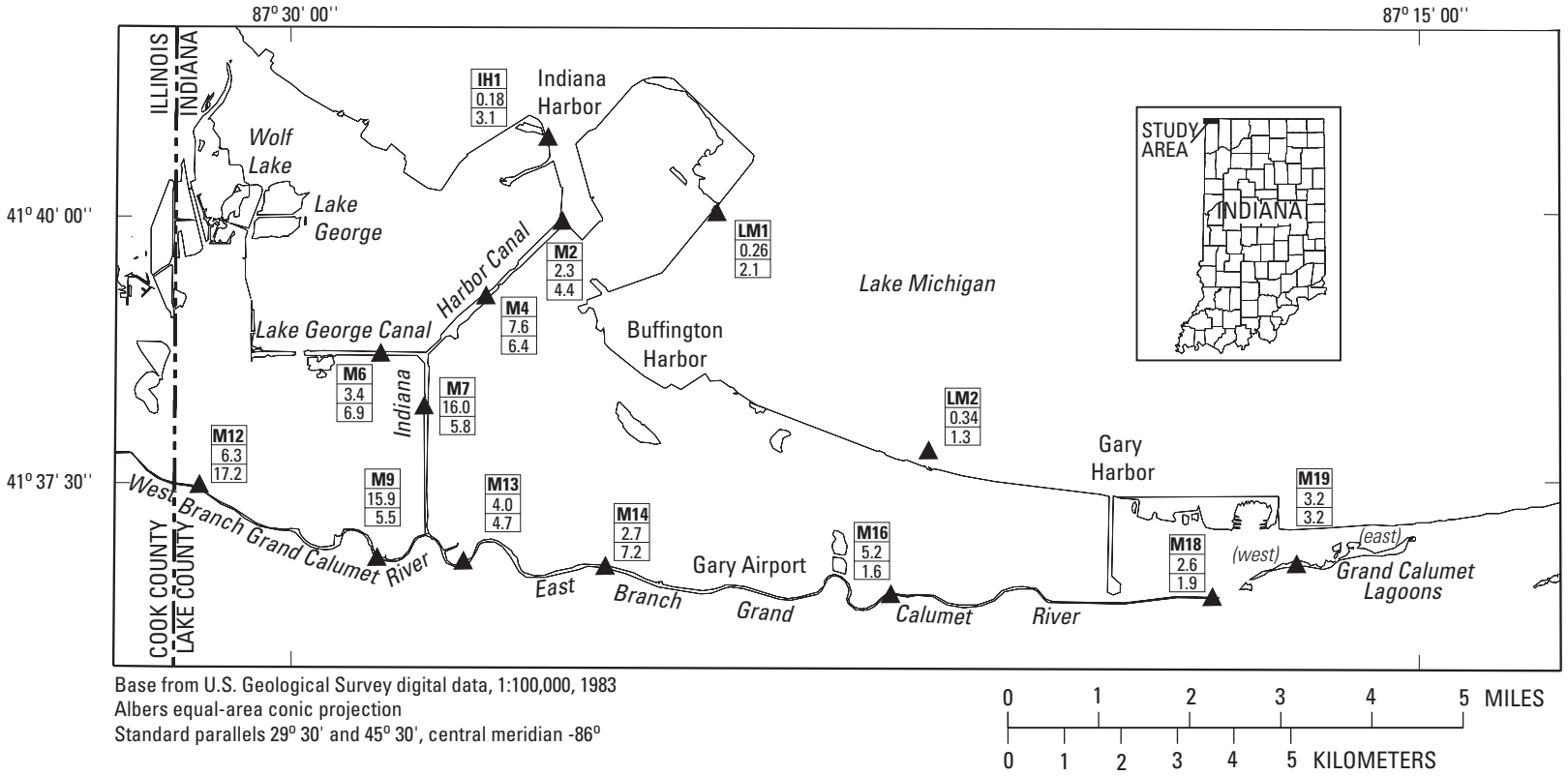
[b]Combined methylmercury is the sum of dissolved and particulate concentrations. Unfiltered methylmercury concentrations assumed equivalent to combined methylmercury at selected locations during May 2002.

Table 6. Ranges of combined methylmercury as a percentage of combined total mercury in water samples from groups of sampling locations on the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001 and May 2002.

[IDs, identifications]

Group of sampling locations and location IDs	Combined methylmercury as a percentage of combined total mercury concentration[a]	
	August 2001	May 2002
East Branch Grand Calumet River (M18, M16, M14, M13)	0.2 - 0.5	0 - 6.2
West Branch Grand Calumet River (M12, M9)	.4 - 1.4	1.1 - 2.7
Indiana Harbor Canal (M7, M6, M4, M2)	.1 - .4	0 - 1.2
Grand Calumet Lagoons, west (M19)	.9	1.4
Lake Michigan near water intakes (IH1, LM1, LM2)	.6 - 1.5	0 - .3

[a]Combined total mercury and combined methylmercury is the sum of dissolved and particulate concentrations. Unfiltered methylmercury concentrations assumed equivalent to combined methylmercury at selected locations during May 2002.



EXPLANATION

▲ SAMPLING LOCATION

M12 SAMPLING-LOCATION IDENTIFICATION

6.3 COMBINED TOTAL MERCURY CONCENTRATION (DISSOLVED AND PARTICULATE, IN NANOGRAMS PER LITER), AUGUST 2001

17.2 COMBINED TOTAL MERCURY CONCENTRATION (DISSOLVED AND PARTICULATE, IN NANOGRAMS PER LITER), MAY 2002

Figure 8. Combined total mercury concentrations in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan in Lake County, Indiana, August 2001 and May 2002.

to the maximum concentration in the Indiana Harbor Canal (16.0 ng/L at M7). The proportion of combined total mercury as combined methylmercury was less than 0.5 percent in the Grand Calumet River/Indiana Harbor Canal, with the exception of M19 (0.9 percent) and M12 (1.4 percent). The largest proportion was in Lake Michigan—1.5 percent at LM1 (appendix: table 1–1).

During May 2002 (fig. 8), the combined total mercury concentrations in all samples from the Grand Calumet River/Indiana Harbor Canal exceeded the Indiana water-quality standard of 1.3 ng/L; the mean concentration was 6.28 ng/L. Combined total mercury at three locations in Lake Michigan was equal to or greater than the standard (1.3–3.1 ng/L). The maximum concentration in the West Branch Grand Calumet River (17.2 ng/L at M12) was larger than the maximum concentration in the East Branch Grand Calumet River (7.2 ng/L at M14) and the Indiana Harbor Canal (6.9 ng/L at M6). The proportion of combined total mercury as combined methylmercury in the Grand Calumet River/Indiana Harbor Canal generally was largest in the East Branch Grand Calumet River headwaters (6.2 percent at M18) and the West Branch Grand Calumet River (2.7 percent at M9) (appendix: table 2–1).

Most of the combined total mercury in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan samples was particulate during August 2001 and May 2002 (table 7), with the exception of one sample from the Grand Calumet Lagoons, west, in 2001 and one sample from Lake Michigan in 2002 (appendixes: table 1–1, table 2–1). Particulate methylmercury was detected in all samples for which it was analyzed during August 2001 and May 2002.

Combined total mercury and methylmercury concentrations in the Grand Calumet River/Indiana Harbor Canal were significantly larger than those in Lake Michigan during August 2001 and May 2002 (Wilcoxon-Mann-Whitney rank-sum test, $p = 0.0001$ for total mercury; $p = 0.004$ for methylmercury)[4]. Total mercury concentrations during August 2001 were not significantly different than those during May 2002 (Wilcoxon-Mann-Whitney rank-sum test, $p= 0.30$), but methylmercury concentrations during May 2002 were significantly larger than those during August 2001 (Wilcoxon-Mann-Whitney rank-sum test, $p = 0.001$).

Mercury in Quality-Control Field-Blank Samples

Quality-control field-blank samples were prepared before and after collecting groups of water samples from the Grand Calumet River/Indiana Harbor Canal and Lake Michigan. During 2001, five field-blank samples were prepared, and analyses detected dissolved total mercury (appendix: table 1–5). The field blanks[5] indicated approximately 0.27 ng/L total mercury in some water samples potentially was from collection, handling, transport, or storage. Dissolved total mercury concentrations were less than five times that of the field blanks[6] (1.35 ng/L) in 11 samples collected during 2001; dissolved concentrations were not used to compute combined total mercury in these 11 samples (appendix: table 1–1). During 2002, six field-blank samples were prepared, and analyses detected total mercury (appendix: table 2–5). The field blanks indicated approximately 0.02 ng/L total mercury potentially was from collection, handling, transport, or storage. Total mercury concentrations were more than five times that of the field blanks (0.1 ng/L) in every sample; all the dissolved and particulate total mercury concentrations were used to compute combined total mercury in these samples for 2002 (appendix: table 2–1).

Table 7. Ranges of particulate total mercury as a percentage of combined total mercury in water samples from groups of sampling locations on the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001 and May 2002.

[IDs, identifications]

Group of sampling locations and location IDs	Particulate total mercury as a percentage of combined total mercury[a] in water samples	
	August 2001	May 2002
East Branch Grand Calumet River (M18, M16, M14, M13)	100	66.2 - 94.8
West Branch Grand Calumet River (M12, M9)	88.8 - 100	76.6 - 89.8
Indiana Harbor Canal (M7, M6, M4, M2)	100	86.0 - 88.6
Grand Calumet Lagoons, west (M19)	26.2	80.6
Lake Michigan near water intakes (IH1, LM1, LM2)	100	47.3 - 85.9

[a]Combined total mercury computed as the sum of dissolved mercury and particulate mercury concentration in a water sample, compared with the particulate total mercury measured in that same sample.

[4]The Wilcoxon-Mann-Whitney rank-sum test (Helsel and Hirsch, 1995) is a nonparametric procedure used to evaluate the distributions of values in two groups. In this statistical analysis, a significance level of 0.05 or less was used to accept a statistical difference in the distributions. The p-value is the significance level attained by the data—the smaller the p-value, the more believable the statistical difference.

[5]Data from field blanks used according to U.S. Environmental Protection Agency (2001b).

[6]Sample concentrations less than five times field-blank concentrations are rejected for use in enforcement of water-quality standards (Indiana Department of Environmental Management, Office of Water Quality, Chemistry Section, written commun., 2001); 0.27 ng/L multiplied by 5 equals 1.35 ng/L.

Factors Affecting Mercury Concentrations and Mercury Transport

This section discusses factors affecting mercury concentrations and mercury transport in the study area. Contrasts in the weather and streamflow between the two sampling periods are described. The relations of suspended sediment, suspended fine particulates, and water-quality constituents to mercury concentrations are discussed. Natural variability in mercury concentrations is examined.

Weather and Streamflow

The study was designed to provide contrasts in weather and streamflow between August 2001 and May 2002 to identify potential seasonal differences in mercury and methylmercury in the Grand Calumet River/Indiana Harbor Canal. As intended, the two sampling periods differed in weather and streamflow.

During sampling in August 2001, weather generally was dry and warm; during sampling in May 2002, weather generally was wet and cool. Records from the weather station at the Indiana Dunes National Lakeshore approximately 10 mi east of the study area (Louis Brenan, National Park Service, 2002, written commun.) were used to summarize weather conditions. Samples were collected August 21–24 and August 28–29, 2001, from the Grand Calumet River/Indiana Harbor Canal. At the Indiana Dunes National Lakeshore, 0.28 in. of rain was recorded August 21–24; no rain fell August 28–29, 2001. The mean air temperature at the Indiana Dunes National Lakeshore weather station August 21–29, 2001, was 22.2°C (71.9°F) and ranged from 13.9 to 30.5°C (57–86.9°F). Samples were collected May 6–9 and May 15, 2002, from the Grand Calumet River/Indiana Harbor Canal. At the Indiana Dunes National Lakeshore, 2.1 in. of rain were recorded May 6–9; 2.6 in. of rain were recorded May 12–15, 2002, even though May 15 was dry. The mean air temperature at the Indiana Dunes National Lakeshore weather station May 6–15, 2002, was 12.2°C (53.9°F) and ranged from 4.4 to 23.4°C (39.9–74.1°F). The mean water temperatures measured at sampling locations on the Grand Calumet River/Indiana Harbor Canal were 26.5°C, August 21–29, 2001, and 16.4°C, May 6–15, 2002.

Streamflow during the time of sampling at six of nine locations on the Grand Calumet River/Indiana Harbor Canal (table 8) was greater in May 2002 than in August 2001. A statistical difference in the distribution of streamflow values was not observed for 2001 and 2002 (Wilcoxon-Mann-Whitney rank-sum test, $p = 0.14$).

Suspended Sediment and Suspended Fine Particulates

Suspended sediment and suspended fine particulates were determined in this study because they could be related to particulate mercury transport in the Grand Calumet River/Indiana Harbor Canal. Organic carbon and plant pigments were determined to estimate the composition of the suspended sediment and suspended fine particulates.

In the Indiana Harbor Canal study by Renn (2000), the mean suspended-sediment concentration for 1,856 samples from 1996 through 1998 was 15 mg/L and the range was 1 to 97 mg/L. Mean suspended-sediment concentration in the Grand Calumet River/Indiana Harbor Canal was 11.4 mg/L in August 2001 and 15.8 mg/L in May 2002. The maximum values in August 2001 (45.3 mg/L; table 8) and May 2002 (32.2 mg/L; table 8) were less than the 97 mg/L maximum for 1996 through 1998.

The mean suspended-sediment concentration in water samples from sampling locations on the Grand Calumet River/Indiana Harbor Canal (table 8) was larger in May 2002 (15.8 mg/L) than in August 2001 (11.4 mg/L). The suspended-sediment concentrations at 7 of 10 sampling locations on the Grand Calumet River/Indiana Harbor Canal were larger in May 2002 than in August 2001. A statistical difference in the distributions of suspended-sediment concentrations in the Grand Calumet River/Indiana Harbor Canal was noted between 2001 and 2002 but at a 0.06 level of significance (Wilcoxon-Mann-Whitney rank-sum test, $p = 0.06$).

The variability of suspended-sediment concentrations in the Grand Calumet River/Indiana Harbor Canal was demonstrated in sequential duplicate samples collected at multiple verticals across the stream channel at five sampling locations in May 2002 (table 9). Suspended-sediment concentrations differed by 2.0 to 54.1 mg/L and the relative percent difference (RPD) was 19 to 132 percent. Another indication of variability in suspended-sediment concentrations was that sequential duplicate samples from location M13 on the East Branch Grand Calumet River in August 2001 differed by 3.7 mg/L, a RPD of 49 percent (appendix: table 1–6).

Suspended-sediment concentrations in water samples from the study area were determined from solids retained on a 1.5-μm pore-size filter. Seston concentrations in water samples from the study area were determined from the ash-free dry weight of solids retained on a 0.7-μm pore-size filter. Seston includes suspended sediments that are solids larger than 1.5 μm and suspended fine particulates that are solids from 0.7 to 1.5 μm. Suspended-fine-particulate concentrations were computed as the difference of seston and suspended-sediment concentrations (appendixes: table 1–3, table 2–3). The proportion of suspended fine particulates of the seston in the water samples from the Grand Calumet River/Indiana Harbor Canal in 2001 and 2002 averaged 11 percent (table 10); no fine particulates were measured in most of the samples.

Table 8. Streamflow at 10 sampling locations and suspended-sediment concentration in water samples, Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001 and May 2002.

[ID, identification; ft^3/s, cubic foot per second; mg/L, milligram per liter; GCR, Grand Calumet River; -- , no data]

Sampling location and ID		Streamflow (ft^3/s)		Suspended-sediment concentration (mg/L)	
		August 2001	May 2002	August 2001	May 2002
M18	East Branch GCR	--	--	8.5	21.6
M16	East Branch GCR	467	446	13.2	7.2
M14	East Branch GCR	529	540	7.1	13.6
M13	East Branch GCR	691	629	9.4	32.1
M12	West Branch GCR	7.9	40	4.7	13.7
M9	West Branch GCR	44.6	159	45.3	12.4
M7	Indiana Harbor Canal	431	580	10.9	15.1
M6	Indiana Harbor Canal	94.2	--	3.2	5.3
M4	Indiana Harbor Canal	551	834	6.2	32.2
M2	Indiana Harbor Canal	578	782	5.8	4.8
	Mean	**377**	**501**	**11.4**	**15.8**

Table 9. Suspended-sediment concentrations in sequential duplicate water samples from five sampling locations on the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, May 2002.

[mg/L, milligram per liter; ID, identification; RPD, relative percent difference; GCR, Grand Calumet River; -- , no data]

Sampling location and ID		Suspended-sediment concentration (mg/L)				
		Vertical 1	Vertical 2	Vertical 3	Maximum difference[a]	RPD[b]
M16	East Branch GCR	7.1	6.3	8.3	2.0	27
M14	East Branch GCR	12.5	15.2	--	2.7	19
M13	East Branch GCR	67.9	18.0	13.8	54.1	132
M9	West Branch GCR	14.2	11.0	--	3.2	25
M7	Indiana Harbor Canal	20.0	18.0	5.5	14.5	114

[a]Maximum difference of concentrations computed by subtracting smallest concentration from largest concentration.

[b]Relative percent difference computed as difference between concentrations divided by the average, multiplied by 100.

Table 10. Proportions of suspended fine particulates, particulate organic carbon, and plant pigments (chlorophyll-a and pheophytin-a) in seston of water samples from groups of sampling locations on the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001 and May 2002.

[IDs, identifications; -- , no data]

Group of sampling locations and location IDs	Proportion of suspended fine particulates (percent)		Proportion of particulate organic carbon (percent)		Proportion of plant pigments (percent)	
	August 2001	May 2002	August 2001	May 2002	August 2001	May 2002
East Branch Grand Calumet River (M18, M16, M14, M13)	0 - 37	0 - 13	0.38 - 2.5	0.80 - 1.3	0.02 - 0.07	0.03 - 0.29
West Branch Grand Calumet River (M12, M9)	0 - 61	0 - 5	.35 - 1.5	.20 - 1.2	.03 - .33	.08
Indiana Harbor Canal (M7, M6, M4, M2)	0	0 - 35	4.3	0 - 15	.02	.04 - .09
Grand Calumet Lagoons, west (M19)	--	0	--	1.1	--	.15
Mean (all locations, 2001 and 2002)	**11**		**2.1**		**.08**	

The seston could include inorganic and organic solids. The proportion of organic solids in the seston was estimated with the concentration of particulate organic carbon. Particulate organic carbon was computed as the difference of total and dissolved organic carbon in water samples from the study area (appendixes: table 1–3, table 2–3). The proportion of particulate organic carbon in the seston of the water samples from the Grand Calumet River/Indiana Harbor Canal in 2001 and 2002 averaged 2.1 percent (table 10). The highest proportion of particulate organic carbon (15 percent) was in the May 2002 sample from M2 in the Indiana Harbor.

The particulate organic carbon could include plants and animals (phytoplankton and zooplankton) and nonliving carbon. An estimate of the plant matter in the seston was made with the sum of the concentrations of two plant pigments (chlorophyll-a and pheophytin-a) from water samples in the study area. The proportion of these two plant pigments in the seston of the water samples from the Grand Calumet River/ Indiana Harbor Canal averaged 0.08 percent (table 10). The highest proportion of plant pigment in the seston was 0.33 percent in the August 2001 sample from M12 in the West Branch Grand Calumet River and 0.29 percent in the May 2002 sample from M18 in the East Branch Grand Calumet River (table 10).

With these data, the estimated composition of most of the suspended solids in the water samples from the Grand Calumet River/Indiana Harbor Canal was sediment larger than 1.5 μm containing approximately 2 percent particulate organic carbon and less than 0.1 percent plant pigment. Sediment larger than 1.5 μm includes medium clay, silt, and sand (Horowitz, 1991).

Natural Variability of Mercury Concentrations

Natural variability of mercury concentrations was demonstrated with 18 total mercury and 9 methylmercury sequential duplicate samples (appendixes: table 1–6, table 2–6). Relative percent difference[7] (RPD) was used to quantify the natural variability. Among the duplicate samples from the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, dissolved total mercury concentrations varied as much as 75.4 percent (median, 44.2 percent); particulate total mercury varied as much as 155.6 percent (median, 24.1 percent); and unfiltered total mercury varied as much as 8.9 percent (median, 2.8 percent). Particulate methylmercury varied as much as 46.2 percent (median, 6.5 percent), and unfiltered methylmercury varied as much as 20.6 percent (median, 9.3 percent).

[7]Relative percent difference (RPD) is a percentage computed by subtracting one concentration from the other and dividing the difference by the average of the two concentrations, then multiplying by 100 to obtain a percentage.

The combined and particulate total mercury concentrations in the Grand Calumet River/Indiana Harbor Canal in 2001 and 2002 were not correlated to suspended-sediment concentrations (Kendall's tau correlation coefficient, p = 0.38 for combined total mercury; p = 0.59 for particulate total mercury).[8]

The natural variability of mercury in water from the study area should be considered when single samples or small data sets are evaluated without duplicate samples for comparison. It is possible that the distribution of suspended sediment and suspended fine particulates (horizontally and vertically in the channel of the Grand Calumet River/Indiana Harbor Canal or vertically in the Grand Calumet Lagoons, west, or Lake Michigan) contributed to the variability of total mercury and methylmercury concentrations in duplicate samples.

Water-Quality Constituents

The largest values of water-quality characteristics and largest concentrations of major ions and nutrients generally were measured in samples from the West Branch Grand Calumet River at sites M9 and M12 and from the East Branch Grand Calumet River headwaters at site M18 (appendixes: table 1–3, table 2–3). The range and maximum concentrations of dissolved solids, total organic carbon, and sulfate are summarized in table 11. Combined total mercury concentrations in 2001 and 2002 were not significantly correlated to concentrations of dissolved solids, total organic carbon, or sulfate (Kendall's tau correlation coefficient, p = 0.16 for dissolved solids; p = 0.38 for total organic carbon; p = 0.35 for dissolved organic carbon; p = 0.40 for sulfate). Combined methylmercury concentrations in 2001 and 2002, however, were significantly correlated to dissolved solids, total organic carbon, and sulfate (Kendall's tau correlation coefficient, p = 0.0008 for dissolved solids; p = 0.004 for total organic carbon; p = 0.0006 for dissolved organic carbon; p = 0.02 for sulfate).

[8]The Kendall's tau correlation coefficient (Helsel and Hirsch, 1995) is a nonparametric, rank-based procedure to evaluate the relation between two variables. In this statistical analysis, a significance level of 0.05 or less was used to accept a statistical relation between the two variables. The p-value is the significance level attained by the data—the smaller the p-value, the more believable the statistical relation.

Total Mercury Loads

Total mercury loads during the time of sampling were estimated with the combined total mercury concentrations in water samples and instantaneous streamflow values concurrent with the hour of water-sample collection at eight locations with streamflow data. Table 12 presents the estimated combined total mercury loads (mg/hr) for the East Branch and West Branch Grand Calumet River and the Indiana Harbor Canal in the study area during August 2001 and May 2002. Estimated instantaneous mercury loads in the Indiana Harbor Canal were as large as 703 mg/hr in August 2001 and 542 mg/hr in May 2002 (fig. 9). The largest loads were in the Indiana Harbor Canal and in the East Branch Grand Calumet River because of more streamflow. Generally, the loads in the Indiana Harbor Canal decreased between M7 and M2 or M4 and M2, indicating that mercury may be deposited with streambed sediment, corresponding to decreases in particulate mercury concentrations (appendixes: table 1–1, table 2–1). A statistical difference was not observed between estimated total mercury loads in August 2001 and May 2002 (Wilcoxon-Mann-Whitney rank-sum test, p = 0.68). Data for the load estimates are in the appendixes (table 1–2, table 2–2).

Table 11. Ranges of concentrations of dissolved solids, total organic carbon, and sulfate in water samples from groups of sampling locations on the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001 and May 2002.

[Concentrations in milligram per liter, mg/L; IDs, identifications; -- , no data]

Group of sampling locations and location IDs	Dissolved solids		Total organic carbon		Sulfate	
	2001	2002	2001	2002	2001	2002
East Branch Grand Calumet River (M18, M16, M14, M13)	216 - 558	206 - 504	2.56 - 8.54	2.12 - 6.81	28.7 - 169	29.8 - 125
West Branch Grand Calumet River (M12, M9)	448 - 818	304 - 492	7.28 - 8.26	6.47 - 6.85	209 - 248	96.3
Indiana Harbor Canal (M7, M6, M4, M2)	194 - 292	254 - 412	2.20 - 3.10	3.32 - 5.24	54.3	42.8 - 63.0
Grand Calumet Lagoons, west (M19)	--	400	10.6	6.65	--	73.2
Lake Michigan near water intakes (IH1, LM1, LM2)	166 - 202	172 - 221	1.92 - 2.52	1.94 - 6.49	--	--

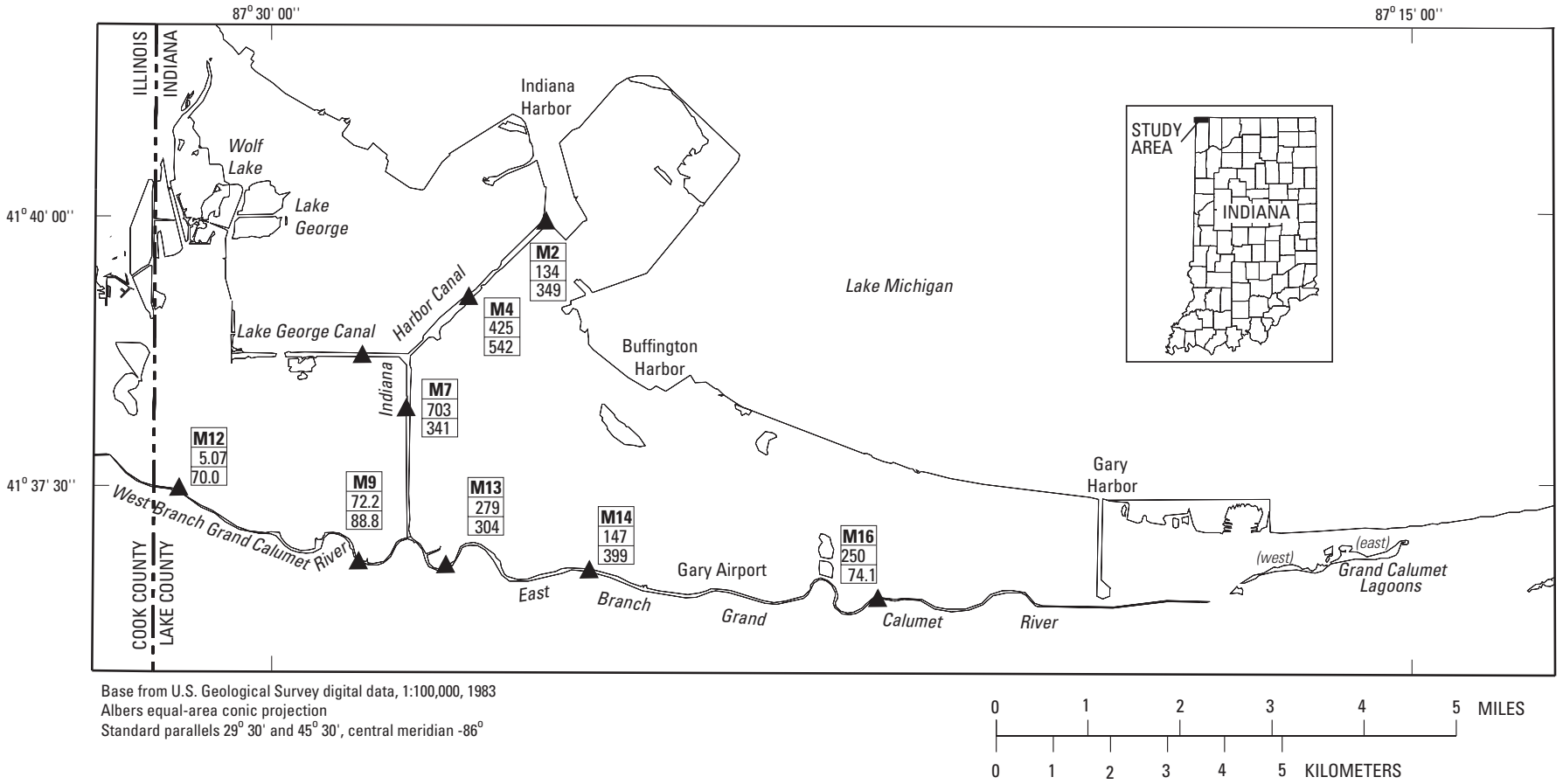


Figure 9. Estimated loads of combined total mercury during the time of sampling at selected locations in the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001 and May 2002.

Table 12. Estimated loads of combined total mercury during the time of sampling at eight sampling locations on the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001 and May 2002.

[mg/hr, milligram per hour; ID, identification; GCR, Grand Calumet River]

Sampling location and ID		Estimated load of combined total mercury[a] (mg/hr)	
		August 2001	May 2002
M16	East Branch GCR	250	74.1
M14	East Branch GCR	147	399
M13	East Branch GCR	279	304
M12	West Branch GCR	5.07	70.0
M9	West Branch GCR	72.2	88.8
M7	Indiana Harbor Canal	703	341
M4	Indiana Harbor Canal	425	542
M2	Indiana Harbor Canal	134	349

[a]Combined total mercury concentrations are a sum of dissolved and particulate concentrations.

Implications for a Total Maximum Daily Load

Data from this study have implications for a Total Maximum Daily Load for mercury in the Grand Calumet River/Indiana Harbor Canal. Comparisons of data from this study with historical data show consistency in a longer time scale. Mercury in effluent samples indicate potential mercury inputs that could be controlled to achieve a TMDL. Mercury in ground-water discharge may be difficult to control to achieve a TMDL because of its diffuse and widespread distribution. Other inputs of mercury to a TMDL are described in this section of the report.

Generally, the combined total mercury loads in the Indiana Harbor Canal decreased as water flowed toward Lake Michigan. The largest concentrations of methylmercury and proportions of total mercury as methylmercury in samples from the East Branch and West Branch Grand Calumet River and in samples from the municipal outfalls on the West Branch Grand Calumet River appear to be related to the location of the wetlands.

Comparisons with Historical Data

Total mercury concentrations (table 13) in water samples collected from the Grand Calumet River/Indiana Harbor Canal by the USGS in July 1999 generally were similar to those collected in August 2001 and May 2002 (Kruskal-Wallis rank-sum test, $p = 0.95$).[9] Larger concentrations were measured in the West Branch Grand Calumet River (M9 and M12) than in the East Branch; the overall range of concentrations were similar for all 3 years.

In comparison with the Lake Michigan Mass Balance Study in 1994 and 1995, the data from 2001 and 2002 in this study had several similarities: (a) mercury concentrations in the Grand Calumet River/Indiana Harbor Canal were larger than those in Lake Michigan; (b) mercury concentrations in the Grand Calumet River/Indiana Harbor Canal exceeded the standard, but those in Lake Michigan did not; (c) mercury was predominantly particulate. These data do not indicate substantial changes in the distribution of mercury in the study area from 1994 through 2002.

Table 13. Concentrations of total mercury in water samples from seven sampling locations on the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, July 1999, August 2001, and May 2002.

[Concentrations in nanogram per liter (ng/L); ID, identification; GCR, Grand Calumet River]

Sampling location and ID		July 1999[a]	August 2001[b]	May 2002[b]
M18	East Branch GCR	7.39	2.56	1.89
M13	East Branch GCR	3.31	3.96	4.74
M12	West Branch GCR	6.23	6.30	17.2
M9	West Branch GCR	19.0	15.9	5.48
M7	Indiana Harbor Canal	5.18	16.0	5.76
M6	Indiana Harbor Canal	2.06	3.42	6.87
M2	Indiana Harbor Canal	3.11	2.28	4.38

[a]Total mercury concentration in unfiltered sample.

[b]Sum of dissolved and particulate total mercury concentrations.

Mercury in Effluent Samples

During August 2001 and May 2002, unfiltered mercury concentrations in treated effluent samples collected by the USGS exceeded the Indiana water-quality standard of 1.3 ng/L for waters in the Great Lakes system at the municipal outfall

[9]The Kruskal-Wallis rank-sum test (Helsel and Hirsch, 1995) is a non-parametric procedure to evaluate if the distributions of the three groups are different. A significance level of 0.05 or less was used to accept a statistical difference in the distributions of the three groups. The p-value is the significance attained by the data—the smaller the p-value, the more believable the statistical difference.

MO2 (10.8 and 2.48 ng/L) and the Indiana Harbor Canal industrial outfall IO1 (2.00 and 3.71 ng/L); the Indiana water-quality standard was not exceeded at the municipal outfall MO1 (0.60 and 1.08 ng/L). Mercury concentrations in sequential duplicate effluent samples varied as much as 121 percent (median, 27.3 percent) (appendixes: tables 1–4 and 1–6, tables 2–4 and 2–6).

IDEM provided total mercury data for unfiltered grab samples from effluent outfalls and water intakes at two industries and one municipality in the study area (Kathy Luther, Indiana Department of Environmental Management, written commun., February 2002, February 2003). These samples were collected at the same time as the USGS samples in 2001 and 2002.

In the data from IDEM for 2001 and 2002, the mean total mercury concentrations in effluent samples were (a) 1.0 ng/L in 2001 from 12 industrial outfalls and 2.5 ng/L in 2002 from 4 industrial outfalls on the East Branch Grand Calumet River; (b) 0.72 ng/L in 2001 from 4 industrial outfalls on the Indiana Harbor Canal; and (c) 1.8 ng/L in 2001 and 12.2 ng/L in 2002 from 1 municipal outfall on the East Branch Grand Calumet River. Also, the mean mercury concentrations in samples from the water-supply intakes were (a) 0.69 ng/L in 2001 and 1.0 ng/L in 2002 for the industrial outfalls on the East Branch Grand Calumet River, and (b) 0.32 ng/L in 2001 for the industrial outfalls on the Indiana Harbor Canal. (The USGS data for mercury in Lake Michigan near these intakes [LM1, LM2; appendixes: tables 1–1, 2–1] ranged from 0.26 to 2.10 ng/L).

The effluent and water-intake data indicated mercury concentrations in industrial and municipal effluent could exceed the Indiana water-quality standard, even when the intake water from Lake Michigan contained mercury concentrations less than the standard. Also, mercury concentrations in municipal effluents were larger and more variable than those in industrial effluent, presenting a potential for larger mercury loads, based on concentration.

Mercury in Ground-Water Discharge

Willoughby and Siddeeq (2001) estimated the maximum loads of mercury in ground water discharging to eight reaches of the Grand Calumet River/Indiana Harbor Canal (fig. 5 and table 14). The maximum instantaneous load of total mercury in surface water (in 2001 or 2002, table 12) for the sampling locations in six of the eight reaches was compared with the estimated maximum load of mercury in ground-water discharge. In these six reaches, the mercury load in surface water was 2.4 to 20.9 percent ground-water discharge. The largest contributions of mercury from ground water were at site M14 (20.9 percent) and site M16 (20 percent) in the East Branch Grand Calumet River and site M12 (11.9 percent) in the West Branch Grand Calumet River. Sites M14 and M12 are near wetlands, and site M16 is downstream from wetlands.

Table 14. Maximum estimated loads of total mercury in ground-water discharges to stream reaches and maximum instantaneous loads of total mercury at eight sampling locations on the Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001 and May 2002.

[ID, identification; mg/hr, milligram per hour; GCR, Grand Calumet River]

Sampling location and ID		Stream reach[a]	Estimated ground-water load: maximum load of total mercury in ground-water discharge (mg/hr)[b]	Estimated surface-water load: maximum instantaneous load of total mercury in surface water (mg/hr)	Ratio of ground-water load to surface-water load (percent)
M16	East Branch GCR	B	50.0	250	20.0
M14	East Branch GCR	C	83.3	399	20.9
M13	East Branch GCR	C	8.3	304	2.7
M12	West Branch GCR	E	8.3	70	11.9
M9	West Branch GCR	D	8.3	89	9.4
M7	Indiana Harbor Canal	F	16.7	703	2.4
M4	Indiana Harbor Canal	H	16.7	542	3.1
M2	Indiana Harbor Canal	H	16.7	349	4.8

[a]Stream reaches are identified on figure 5.

[b]Maximum estimated loads from Willoughby and Siddeeq (2001, p. 35) were in kilograms per day and were converted to an equivalent milligrams per hour for table 14.

Inputs of Mercury

Data are needed to determine the proportional inputs of mercury to the Grand Calumet River/Indiana Harbor Canal that contribute to a TMDL. Some of these data were provided through this study; other data sources are identified in this discussion.

- **Treated Effluent.** Mercury concentrations from municipal and industrial outfalls were obtained during this study; discharge volumes can be estimated from municipal and industrial records.
- **Ground Water.** Estimated mercury loading from ground-water discharge to eight reaches of the Grand Calumet River/Indiana Harbor Canal (Willoughby and Siddeeq, 2001) were based on mercury concentrations determined in ground-water samples in the study area (Duwelius and others, 1996).
- **Atmospheric Deposition.** Seasonal and annual total mercury wet-deposition data from the NADP Mercury Deposition Network station at the Indiana Dunes National Lakeshore can be used to estimate atmospheric deposition to the Grand Calumet River Basin.
- **Noncontact Industrial Effluent.** Mercury concentrations from Lake Michigan near or in the water-supply intakes may represent mercury in noncontact industrial effluent. These data were obtained during this study and compared with historical data.
- **Stormwater Runoff.** This input of mercury potentially could be inferred from atmospheric deposition and a runoff coefficient or with data on flow and mercury concentrations in samples from storm sewers and combined-sewer overflows during storms.
- **Contaminated Sediment.** This input of mercury could be estimated with concentrations in sediment. Releases from contaminated sediment potentially could be inferred by mass balance with data on the total mercury load and the proportional input from the other sources.

Summary and Conclusions

The Grand Calumet River/Indiana Harbor Canal was first on the IDEM list of water bodies scheduled for development of a TMDL for mercury under provisions of the Clean Water Act section 303(d). A TMDL, if developed, could be used by IDEM to limit mercury discharges from permitted point sources in an effort to achieve the Indiana water-quality standard of 1.3 ng/L total mercury for waters within the Great Lakes system. The mercury TMDL required a base line of data with mercury reporting limits less than 1.3 ng/L, but few reliable data were available. IDEM requested that the USGS obtain data on the occurrence and distribution of mercury in the Grand Calumet River/Indiana Harbor Canal and near-shore Lake Michigan with ultra-clean sampling protocols and low-level analytical methods.

The USGS collected samples during warm, dry weather in summer 2001 and cool, wet weather in spring 2002 that provided a contrast in streamflow conditions and seasonal extremes of historical suspended-sediment concentrations. Total mercury and methylmercury were analyzed in water samples. Sets of filtered and particulate samples were collected to estimate mercury partitioning between water and particulates. To evaluate the types of particulates potentially transporting mercury, supplementary constituents were analyzed to estimate the size, organic-carbon content, and plant-pigment content of particulates in the water. Comparability of the mercury data was promoted by: (1) sample collection during short-duration time periods; (2) streamflow measurements for comparison of hydrologic conditions; (3) use of the same field equipment, supplies, sampling procedures, personnel, and analytical laboratory for all samples.

Total mercury concentrations in all the Grand Calumet River/Indiana Harbor Canal samples exceeded the Indiana water-quality standard. Most total mercury concentrations in the Grand Calumet River/Indiana Harbor Canal were larger than those in Lake Michigan. Total mercury and methylmercury concentrations were larger in more samples collected during the wet-weather streamflow conditions during May 2002 than in samples collected during the dry-weather streamflow conditions during August 2001. The largest total mercury concentrations were in the West Branch Grand Calumet River near wetlands and municipal outfalls (17.2 ng/L) and in the Indiana Harbor Canal near the confluence of the East Branch and West Branch Grand Calumet River (16.0 ng/L).

Methylmercury was no more than 1.5 percent of the total mercury concentration in August 2001 and no more than 6.2 percent in May 2002. Methylmercury concentrations were correlated with concentrations of dissolved solids, total organic carbon, and sulfate.

Particulate total mercury was the predominant form of total mercury detected in the Grand Calumet River/Indiana Harbor Canal, and nearly all methylmercury detected was particulate. The estimated composition of most of the particulates in the water samples from the Grand Calumet River/Indiana Harbor Canal was sediment larger than medium clay containing less than 2 percent particulate organic carbon and less than 0.08 percent plant pigment.

Estimated instantaneous total mercury loads in the Indiana Harbor Canal were as large as 703 mg/hr in August 2001 and 542 mg/hr in May 2002. As much as 21 percent of the instantaneous mercury load in some stream reaches could have been from ground-water discharge. Municipal effluent had larger and

more variable mercury concentrations than industrial effluent and presents a potential for larger mercury loads, based on concentration.

This study adds to a base line of data about mercury in the Grand Calumet River/Indiana Harbor Canal. Comparisons of data from this study with historical data indicate that substantial changes in mercury concentrations and mercury transport in the study area probably have not occurred from 1994 through 2002. Data are needed to determine the proportional inputs of mercury to the Grand Calumet River/Indiana Harbor Canal from all the sources that contribute to a TMDL.

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Appendixes 1–3.

Table 1–1. Total mercury and methylmercury concentrations, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001.

[ID, identification; ng/L, nanogram per liter; < , less than reporting limit listed; GCR, Grand Calumet River; IHC, Indiana Harbor Canal]

		Dissolved total mercury								
	Sampling-location ID and name	Sample concentration (ng/L)	Detection limit (ng/L)	Particulate total mercury[a] (ng/L)	Combined[b] total mercury (ng/L)	Dissolved[c] methylmercury (ng/L)	Particulate[c] methylmercury (ng/L)	Combined[b] methylmercury (ng/L)	Combined methylmercury to combined total mercury (percent)	Particulate total mercury to combined total mercury (percent)
M19	Grand Calumet Lagoons, west	2.34[d]	0.004	0.83	3.17	<0.001	0.030	0.030	0.9	26.2
M18	East Branch GCR headwaters	.53[e, f]	.008	2.56[e]	2.56	<.001[e]	.013[e]	.013	.5	100
M16	East Branch GCR at Bridge St.	.69[f]	.004	5.25	5.25	<.001	.013	.013	.2	100
M14	East Branch GCR at Cline Ave.	.65[f]	.025	2.72	2.72	<.001	.008	.008	.3	100
M13	East Branch GCR at Kennedy Ave.	.58[e, f]	.025	3.96[e]	3.96	<.001[e]	.012[e]	.008	.3	100
M12	West Branch GCR at Hohman Ave.	.59[f]	.004	6.30	6.30	.045	.046	.091	1.4	100
M9	West Branch GCR at Indianapolis Blvd.	1.78[e]	.008	14.1[e]	15.9	<.001[e]	.057[e]	.050	.4	88.8
M7	IHC at Columbus Dr.	.42[f]	.008	16.0	16.0	<.001	.015	.015	.1	100
M6	IHC at Lake George Canal	.80[f]	.008	3.42	3.42	<.001	.012	.012	.4	100
M4	IHC at Dickey Rd.	1.26[e]	.004	7.56[e]	7.56	<.001[e]	.024[e]	.015	.3	100
M2	IHC at mouth of Indiana Harbor	.51[f]	.025	2.28	2.28	<.001	.010	.010	.4	100
IH1	Indiana Harbor near industrial intake	.47[e, f]	.008	.18	.18	<.001[e]	.001[e]	.001	.6	100
LM1	Lake Michigan near industrial intake 1	.52[f]	.004	.26	.26	<.001	.004	.004	1.5	100
LM2	Lake Michigan near industrial intake 2	.45[f]	.004	.34	.34	<.001[e]	.004[e]	.004	1.2	100

[a]Detection limit for particulate total mercury was 0.03 nanogram per liter for all samples.

[b]Combined total mercury and combined methylmercury computed as sum of dissolved and particulate concentrations except for footnote "f" below.

[c]Detection limit for dissolved and particulate methylmercury was 0.001 nanogram per liter for all samples.

[d]Estimated concentration; more than 5 times and less than 10 times the mean concentration in five field blanks (table 1–5).

[e]Concentration in one of two sequentially collected field duplicate samples.

[f]Concentration was less than five times the mean concentration in five field blanks (table 1–5). Not used to compute combined total mercury concentration.

Table 1–2. Estimated loads of combined total mercury during the time of sampling at eight sampling locations, Grand Calumet River/ Indiana Harbor Canal, Lake County, Indiana, August 2001.

[ID, identification; hour start and end in military time; ft^3/s, cubic foot per second; total mercury concentration is a sum of dissolved and particulate total mercury concentrations; ng/L, nanogram per liter; mg/hr, milligram per hour; ADCP, acoustic Doppler current profiler]

Sampling-location ID and name	Date for mercury-load estimate	Hour for mercury-load estimate	Streamflow (ft^3/s)	Source of streamflow data	Combined total mercury concentration[a] (ng/L)	Load[b] of combined total mercury (mg/hr)
East Branch Grand Calumet River						
M16 (at Bridge St.)	8/21/01	1500–1600	467	Tethered ADCP[c]	5.25	250
M14 (at Cline Ave.)	8/22/01	1130–1230	529	Tethered ADCP[c]	2.72	147
M13 (at Kennedy Ave.)	8/22/01	1700–1800	691	Tethered ADCP[c]	3.96[d]	279
West Branch Grand Calumet River						
M12 (at Hohman Ave.)	8/23/01	1530–1530	7.9	Streamflow-gaging station[e]	6.30	5.07
M9 (at Indianapolis Blvd.)	8/23/01	1100–1200	44.6	Current meter	15.9[d]	72.2
Indiana Harbor Canal						
M7 (at Columbus Dr.)	8/20/01	1800–1900	431	Streamflow-gaging station[f]	16.0	703
M4 (at Dickey Rd.)	8/28/01	1230–1330	551	Streamflow-gaging station[f]	7.56[d]	425
M2 (at mouth of Indiana Harbor)	8/29/01	1130–1230	578	Streamflow-gaging station[f]	2.28	134

[a]Combined total mercury computed as sum of dissolved total mercury and particulate total mercury concentrations (table 1–1).

[b]Combined total mercury load calculated as product of streamflow, total mercury concentration, and a conversion factor (0.101941). Calculations made with unrounded values and presented with three significant digits for the hour of sample collection.

[c]Streamflow calculated for time of sampling as mean of discharge measured during 4 to 14 stream transects with tethered acoustic Doppler current profiler.

[d]Concentration in one of two sequential duplicate samples.

[e]U.S. Geological Survey streamflow-gaging station 05536357 on West Branch Grand Calumet River at Hohman Ave. Streamflow calculated for hour of sampling from single value for stream stage with stage-discharge method.

[f]U.S. Geological Survey streamflow-gaging station 04092750 on Indiana Harbor Canal at former Canal St. bridge site—upstream from Dickey Rd. (M4) and downstream from confluence with Lake George Canal. Gage used acoustic Doppler velocity meter; streamflow computed with index-velocity method. Streamflow calculated for hour of sampling as mean of four quarter-hour instantaneous streamflow values.

Table 1–3. Water-quality characteristics, physical properties, and major ions, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001.

[ID, identification; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; ntu, nephelometric turbidity unit; n.a., not analyzed; GCR, Grand Calumet River; IHC, Indiana Harbor Canal; µg/L, microgram per liter; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; < , less than reporting limit listed; E, estimated concentration]

	Sampling-location ID and name	pH (s.u.)	Dissolved oxygen (mg/L)	Water temperature (°C)	Specific conductance (µS/cm)	Turbidity (ntu)	Suspended sediment[a] (mg/L)	Seston ash-free dry mass[b] (mg/L)	Suspended sediment to seston ratio[c] (percent)
M19	Grand Calumet Lagoons, west	8.4	13.0	23.5	560	17.3	14.7	n.a.	n.a.
M18	East Branch GCR headwaters	7.3	4.7	20.0	1,100	19.3	8.5	13.4	63
M16	East Branch GCR at Bridge St.	8.2	7.6	29.0	368	13.9	13.2	10.6	100
M14	East Branch GCR at Cline Ave.	7.9	6.3	28.5	409	3.8	7.1	n.a.	n.a.
M13	East Branch GCR at Kennedy Ave.	8.0	6.5	29.5	407	3.6	9.4	9.3	100
M12	West Branch GCR at Hohman Ave.	7.4	6.5	26.0	1,300	2.5	4.7	12.0	39
M9	West Branch GCR at Indianapolis Blvd.	7.1	6.1	24.0	1,250	3.8	45.3	11.3	100
M7	IHC at Columbus Dr.	7.9	6.6	29.0	474	n.a.	10.9	10.6	100
M6	IHC at Lake George Canal	7.7	5.4	28.0	494	5.0	3.2	n.a.	n.a.
M4	IHC at Dickey Rd.	7.6	4.4	28.0	495	7.3	6.2	n.a.	n.a.
M2	IHC at mouth of Indiana Harbor	8.0	6.6	26.0	369	6.9	5.8	n.a.	n.a.
IH1	Indiana Harbor near industrial intake	8.1	6.6	28.5	362	1.1	1.4	n.a.	n.a.
LM1	Lake Michigan near industrial intake 1	8.2	7.0	22.5	316	1.9	1.1	n.a.	n.a.
LM2	Lake Michigan near industrial intake 2	8.2	7.8	22.5	295	2.2	3.6	n.a.	n.a.

Table 1–3. Water-quality characteristics, physical properties, and major ions, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001.—Continued

[ID, identification; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; ntu, nephelometric turbidity unit; n.a., not analyzed; GCR, Grand Calumet River; IHC, Indiana Harbor Canal; µg/L, microgram per liter; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; < , less than reporting limit listed; E, estimated concentration]

Sampling-location ID	Dissolved solids (mg/L)	Dissolved organic carbon (mg/L)	Total organic carbon (mg/L)	Particulate organic carbon[d] (mg/L)	Particulate carbon to seston ratio[e] (percent)	Chlorophyll-a (µg/L)	Pheophytin-a (µg/L)	Plant pigment to seston ratio[f] (percent)	Dissolved calcium (mg/L)	Dissolved magnesium (mg/L)	Dissolved sodium (mg/L)
M19	342	10.3	10.6	0.30	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
M18	558	8.45	8.54	.09	.67	6.06	2.88	.07	95.7	26.8	35.7
M16	216	2.52	2.56	.04	.38	2.11	1.41	.03	38.9	15.2	10.1
M14	224	2.78	2.61	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
M13	232	3.19	2.96	0	0	.82	.60	.02	41.6	14.7	15.0
M12	818	8.44	8.26	0	0	33.4	5.91	.33	65.9	60.4	101
M9	778	7.24	7.28	.04	.35	1.72	1.30	.03	67.4	51.8	96.6
M7	287	3.56	3.10	0	0	.92	1.22	.02	43.9	16.6	20.6
M6	286	2.92	3.01	.09	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
M4	292	2.79	2.78	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
M2	194	2.28	2.20	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
IH1	202	2.44	2.52	.08	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
LM1	170	1.94	2.02	.08	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
LM2	166	1.90	1.92	.02	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table 1–3. Water-quality characteristics, physical properties, and major ions, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001.—Continued

[ID, identification; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; ntu, nephelometric turbidity unit; n.a., not analyzed; GCR, Grand Calumet River; IHC, Indiana Harbor Canal; µg/L, microgram per liter; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; < , less than reporting limit listed; E, estimated concentration]

Sampling-location ID	Dissolved potassium (mg/L)	Dissolved iron (µg/L)	Dissolved manganese (µg/L)	Dissolved alkalinity as $CaCO_3$ (mg/L)	Dissolved chloride (mg/L)	Dissolved sulfate (mg/L)	Dissolved fluoride (mg/L)	Dissolved silica as SiO_2 (mg/L)	Dissolved ortho-phosphate (mg/L)
M18	6.1	117	434	273	76.9	169	0.87	20	<0.02
M16	2.7	<10	7	108	27.2	28.7	.47	1.2	<.02
M13	4.0	13	11	107	35.6	40.4	.45	1.7	.01E
M12	11.1	93	19	139	148	248	.98	4.9	.64E
M9	11.1	77	6	134	152	209	.99	7.5	1.0 E
M7	5.1	18	12	111	45.4	54.3	.52	2.2	.05E

[a]Suspended sediment includes solids retained on a 1.5-micrometer filter.

[b]Seston includes suspended sediment and suspended fine particulates retained on a 0.7-micrometer filter.

[c]Ratio computed as suspended sediment divided by seston, expressed as percent; value larger than 100 percent displayed as 100.

[d]Particulate organic carbon computed as total organic carbon minus dissolved organic carbon; negative difference displayed as zero.

[e]Ratio computed as particulate organic carbon divided by seston, expressed as percent; zero ratio indicates zero particulate organic carbon.

[f]Ratio computed as sum of chlorophyll-a and pheophytin-a divided by seston ash-free dry mass, expressed as percent.

Table 1–4. Unfiltered total mercury and water-quality characteristics of effluent samples, Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, August 2001.

[ID, identification; ng/L, nanogram per liter; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; GCR, Grand Calumet River; IHC, Indiana Harbor Canal]

Sampling-location ID and name		Unfiltered total mercury (ng/L)	pH (s.u.)	Dissolved oxygen (mg/L)	Water temperature (°C)	Specific conductance (µS/cm)
MO1	West Branch GCR municipal outfall 1	0.60	7.1	7.1	24.0	1,220
MO2	West Branch GCR municipal outfall 2	10.8[a]	7.3	7.9	23.5	1,180
IO1	IHC industrial outfall	2.00[a]	8.2	3.0	35.0	562

[a]Concentration in one of two sequential duplicate samples.

Table 1–5. Total mercury in field-blank samples, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001.

[ID, identification; ng/L, nanogram per liter; dissolved methylmercury was analyzed but not detected in any sample; -- , does not apply]

Sample ID	Dissolved total mercury (ng/L)	Blank-corrected dissolved total mercury (ng/L)	Explanation
FB1	0.43	0.27	Blank-corrected concentration of mercury in filtered, pumped field blank was computed by subtracting 0.16 ng/L[a].
FB2	.65	.49	Same as above.
FB3	.26	.10	Same as above.
FB4	.22	.06	Same as above.
FB5	.61	.45	Same as above.
Mean	**--**	**.27**	Mean blank-corrected dissolved total mercury concentration in five field blanks.

[a]Blank correction is sum of mercury in blank water (0.1 nanogram per liter) and mercury added from acid preservative (0.06 nanogram per liter). The U.S. Geological Survey Mercury Research Laboratory's long-term total mercury concentration in the blank water was 0.1 nanogram per liter. Maximum concentration of mercury added to blank water from acid preservative (0.06 nanogram per liter) was based on 1.55-nanogram-per-liter mercury remaining in preservative after field use, diluted at 20-milliliter acid per 500-milliliter sample.

Table 1–6. Variability of selected constituents in sequential duplicate samples, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001.

[ID, identification; ng/L, nanogram per liter; RPD, relative percent difference; n.a., not analyzed; mg/L, milligram per liter]

Sampling-location ID	Dissolved total mercury (ng/L)				Sampling-location ID	Particulate total mercury (ng/L)				Sampling-location ID	Particulate methylmercury (ng/L)			
	First sample	Second sample	Difference[a]	RPD[b]		First sample	Second sample	Difference[a]	RPD[b]		First sample	Second sample	Difference[a]	RPD[b]
M18	0.46	0.53	0.07	14.1	M18	2.56	0.32	2.24	155.6	M18	0.013	0.013	0	0
M13	.49	.58	.09	16.8	M13	3.96	3.63	.33	8.70	M13	.008	.012	.004	40
M9	.85	1.78	.93	70.7	M9	9.79	14.1	4.27	35.8	M9	.050	.057	.007	13.1
M4	1.26	.57	.69	75.4	M4	5.80	7.55	1.75	26.2	M4	.015	.024	.009	46.2
IH1	.30	.47	.17	44.2	IH1	.17	.18	.01	5.70	IH1	.001	.001	0	0
LM2	n.a.	n.a.	n.a.	n.a.	LM2	.30	.34	.04	12.5	LM2	.004	.004	0	0

Sampling-location ID	Unfiltered total mercury (ng/L)				Sampling-location ID	Suspended sediment (mg/L)				Sampling-location ID	Total organic carbon (mg/L)			
	First sample	Second sample	Difference[a]	RPD[b]		First sample	Second sample	Difference[a]	RPD[b]		First sample	Second sample	Difference[a]	RPD[b]
MO2	2.65	10.79	8.14	121.1	M13	9.4	5.7	3.7	49.0	M13	3.0	3.1	0.1	3.3
IO1	2.00	1.52	.48	27.3	LM2	3.6	4.0	.4	10.5	LM2	1.9	2.0	.1	5.1

[a]Difference between concentration of first sample and concentration of second sample.

[b]Relative percent difference is the difference of the two concentrations divided by the average of the concentrations, expressed as percent (for comparative purposes).

Table 2–1. Total mercury and methylmercury concentrations, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, May 2002.

[ID, identification; ng/L, nanogram per liter; < , less than reporting limit listed; GCR, Grand Calumet River; n.a., not analyzed; IHC, Indiana Harbor Canal]

Sampling-location ID and name		Dissolved total mercury		Particulate[a] total mercury (ng/L)	Combined[b] total mercury (ng/L)	Dissolved[c] methyl-mercury (ng/L)	Particulate[d] methyl-mercury (ng/L)	Combined[b] methyl-mercury (ng/L)	Combined methyl-mercury to combined total mercury (percent)	Particulate total mercury to combined total mercury (percent)
		Sample concen-tration (ng/L)	Detection limit (ng/L)							
M19	Grand Calumet Lagoons, west	0.62	0.006	2.59	3.21	<0.002	0.046	0.046	1.4	80.6
M18	East Branch GCR headwaters	.64	.005	1.25	1.89	.069	.048	.117[f]	6.2	66.2
M16	East Branch GCR at Bridge St.	.26	.005	1.37	1.63	n.a.	n.a.	<.002[e]	0	83.9
M14	East Branch GCR at Cline Ave.	.37	.005	6.88	7.25	n.a.	n.a.	<.002[e]	0	94.8
M13	East Branch GCR at Kennedy Ave.	.42	.005	4.32	4.74	n.a.	n.a.	<.002[e]	0	91.1
M12	West Branch GCR at Hohman Ave.	1.76	.005	15.4	17.2	n.a.	n.a.	.181	1.1	89.8
M9	West Branch GCR at Indianapolis Blvd.	1.28	.006	4.20	5.48	<.002	.147	.147[f]	2.7	76.6
M7	IHC at Columbus Dr.	.81	.005	4.95	5.76	<.002	.068	.068[f]	1.2	86.0
M6	IHC at Lake George Canal	.95	.004	5.92	6.87	n.a.	n.a.	.042[e]	.6	86.2
M4	IHC at Dickey Rd.	.76	.004	5.62	6.38	n.a.	n.a.	.046[e]	.7	88.0
M2	IHC at mouth of Indiana Harbor	.50	.003	3.88	4.38	n.a.	n.a.	<.002[e]	0	88.6
IH1	Indiana Harbor near industrial intake	.43	.004	2.63	3.06	n.a.	n.a.	<.002[e, f]	0	85.9
LM1	Lake Michigan near industrial intake 1	.45	.004	1.65	2.10	n.a.	n.a.	<.002[e]	0	78.6
LM2	Lake Michigan near industrial intake 2	.69	.004	.62	1.31	<.002	.004	.004	.3	47.3

[a]Detection limit for particulate total mercury was 0.03 nanogram per liter for all samples.

[b]Combined total mercury and combined methylmercury computed as sum of dissolved and particulate concentrations.

[c]Detection limit for dissolved methylmercury was 0.002 nanogram per liter for all samples.

[d]Detection limit for particulate methylmercury was 0.001 nanogram per liter for all samples.

[e]Unfiltered sample—detection limit was 0.002 nanogram per liter for unfiltered methylmercury.

[f]Concentration in one of two sequentially collected duplicate samples.

Table 2–2. Estimated loads of combined total mercury during the time of sampling at eight sampling locations, Grand Calumet River/ Indiana Harbor Canal, Lake County, Indiana, May 2002.

[ID, identification; hour start and end in military time; ft^3/s, cubic foot per second; ng/L, nanogram per liter; mg/hr, milligram per hour; ADCP, acoustic Doppler current profiler]

Sampling-location ID and name	Date for mercury-load estimate	Hour for mercury-load estimate	Streamflow (ft^3/s)	Source of streamflow data	Combined total mercury concentration[a] (ng/L)	Load[b] of combined total mercury (mg/hr)
East Branch Grand Calumet River						
M16 (at Bridge St.)	5/07/02	1500–1600	446	Tethered ADCP[c]	1.63	74.1
M14 (at Cline Ave.)	5/08/02	0930–1030	540	Current meter	7.25	399
M13 (at Kennedy Ave.)	5/08/02	1430–1530	629	Tethered ADCP[c]	4.74	304
West Branch Grand Calumet River						
M12 (at Hohman Ave.)	5/09/02	1200–1300	40	Streamflow-gaging station[d]	17.2	70.0
M9 (at Indianapolis Blvd.)	5/09/02	1000–1100	159	Current meter	5.48	88.8
Indiana Harbor Canal						
M7 (at Columbus Dr.)	5/06/02	1630–1730	580	Streamflow-gaging station[e]	5.76	341
M4 (at Dickey Rd.)	5/15/02	1500–1600	834	Streamflow-gaging station[e]	6.38	542
M2 (at mouth of Indiana Harbor)	5/15/02	1700–1800	782	Streamflow-gaging station[e]	4.38	349

[a]Total mercury concentration is a sum of dissolved and particulate total mercury concentrations.

[b]Mercury load calculated as product of streamflow, total mercury concentration, and a conversion factor (0.101941). Calculations made with unrounded values and presented with three significant digits for the hour of sample collection.

[c]Streamflow calculated for time of sampling as mean of discharge measured during 4 to 14 stream transects with tethered acoustic Doppler current profiler.

[d]U.S. Geological Survey streamflow-gaging station 05536357 on West Branch Grand Calumet River at Hohman Ave. Streamflow calculated for hour of sampling from single value for stream stage with stage-discharge method.

[e]U.S. Geological Survey streamflow-gaging station 04092750 on Indiana Harbor Canal at former Canal St. bridge site—upstream from Dickey Rd. (M4) and downstream from confluence with Lake George Canal. Gage used acoustic Doppler velocity meter; streamflow computed with index-velocity method. Streamflow calculated for hour of sampling as mean of four quarter-hour instantaneous streamflow values.

Table 2–3. Water-quality characteristics, physical properties, and major ions, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, May 2002.

[ID, identification; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; ntu, nephelometric turbidity unit; GCR, Grand Calumet River; IHC, Indiana Harbor Canal; µg/L, microgram per liter; n.a., not analyzed; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; < , less than reporting limit listed; E, estimated concentration]

	Sampling-location ID and name	pH (s.u.)	Dissolved oxygen (mg/L)	Water temper-nature (°C)	Specific conduct-dance (µS/cm)	Turbidity (ntu)	Suspended sediment[a] (mg/L)	Seston ash-free dry mass[b] (mg/L)	Suspended sediment to seston ratio[c] (percent)
M19	Grand Calumet Lagoons, west	7.9	8.3	16.5	639	12.0	16.8	16	100
M18	East Branch GCR headwaters	7.3	5.2	14.5	851	16.2	21.6	3.3	100
M16	East Branch GCR at Bridge St.	8.1	9.6	17.5	356	.3	7.2	8.3	87
M14	East Branch GCR at Cline Ave.	7.7	7.9	17.0	442	21.6	13.6	8.6	100
M13	East Branch GCR at Kennedy Ave.	7.6	7.4	17.0	491	11.7	32.1	10	100
M12	West Branch GCR at Hohman Ave.	7.2	1.5	16.5	500	15.3	13.7	10	100
M9	West Branch GCR at Indianapolis Blvd.	7.2	6.2	15.5	813	8.9	12.4	13	95
M7	IHC at Columbus Dr.	7.3	6.7	18.0	597	8.8	15.1	10	100
M6	IHC at Lake George Canal	7.3	6.4	17.5	686	7.0	5.3	7.6	70
M4	IHC at Dickey Rd.	7.3	5.3	17.5	683	8.0	32.2	7.6	100
M2	IHC at mouth of Indiana Harbor	7.7	8.8	12.5	378	6.5	4.8	7.4	65
IH1	Indiana Harbor near industrial intake	7.8	6.8	15.5	386	4.0	2.0	6.7	30
LM1	Lake Michigan near industrial intake 1	8.2	8.6	11.5	330	3.6	1.1	6.3	17
LM2	Lake Michigan near industrial intake 2	8.0	9.8	11.0	270	4.9	4.4	5.6	79

Table 2–3. Water-quality characteristics, physical properties, and major ions, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, May 2002.—Continued

[ID, identification; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; ntu, nephelometric turbidity unit; GCR, Grand Calumet River; HC, Indiana Harbor Canal; µg/L, microgram per liter; n.a., not analyzed; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; < , less than reporting limit listed; E, estimated concentration]

Sampling-location ID	Dissolved solids (mg/L)	Dissolved organic carbon (mg/L)	Total organic carbon (mg/L)	Particulate organic carbon[d] (mg/L)	Particulate carbon to seston ratio[e] (percent)	Chlorophyll-a (µg/L)	Pheophytin-a (µg/L)	Plant pigment to seston ratio[f] (percent)	Dissolved calcium (mg/L)	Dissolved magnesium (mg/L)	Dissolved sodium (mg/L)
M19	400	6.48	6.65	0.17	1.1	14.96	8.97	0.15	71.9	24.7	22.8
M18	504	6.75	6.81	.06	1.8	5.00	4.42	.29	86.2	25.2	29.3
M16	206	2.05	2.12	.07	.8	1.35	1.27	.03	35.3	15.3	11.3
M14	253	2.92	3.03	.11	1.3	2.19	1.92	.05	n.a.	n.a.	n.a.
M13	286	3.19	3.27	.08	.8	1.70	1.96	.04	43.7	15.9	26.6
M12	304	6.83	6.85	.02	.2	4.61	3.08	.08	n.a.	n.a.	n.a.
M9	492	6.32	6.47	.15	1.2	6.49	4.48	.08	54.7	17.1	76.4
M7	359	4.07	4.22	.15	1.5	2.70	2.88	.06	49.2	17.0	42.3
M6	412	5.30	5.24	0	0	4.34	2.35	.09	n.a.	n.a.	n.a.
M4	406	4.64	4.83	.19	2.5	2.33	1.54	.05	n.a.	n.a.	n.a.
M2	254	2.24	3.32	1.08	14.6	1.84	1.19	.04	42.3	14.1	22.1
IH1	221	3.23	3.25	.02	.3	1.04	.59	.02	n.a.	n.a.	n.a.
LM1	203	1.93	1.94	.01	.2	1.34	.76	.03	n.a.	n.a.	n.a.
LM2	172	1.88	6.49	4.61	82.3	1.47	1.37	.05	n.a.	n.a.	n.a.

Table 2–3. Water-quality characteristics, physical properties, and major ions, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, May 2002.—Continued

[ID, identification; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; ntu, nephelometric turbidity unit; GCR, Grand Calumet River; IHC, Indiana Harbor Canal; µg/L, microgram per liter; n.a., not analyzed; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; < , less than reporting limit listed; E, estimated concentration]

Sampling-location ID	Dissolved potassium (mg/L)	Dissolved iron (µg/L)	Dissolved manganese (µg/L)	Dissolved alkalinity as $CaCO_3$ (mg/L)	Dissolved chloride (mg/L)	Dissolved sulfate (mg/L)	Dissolved fluoride (mg/L)	Dissolved silica as SiO_2 (mg/L)	Dissolved ortho-phosphate (mg/L)
M19	5.0	220	74.3	198	49.9	73.2	0.61	1.2	<0.02
M18	5.2	303	291	241	59.4	125	.80	9.5	<.02
M16	2.5	7.6	8.4	110	23.7	29.8	.57	1.6	.02
M13	4.0	22.6	23.4	113	46.5	48.1	.57	2.9	.01E
M9	6.2	57.5	15.5	126	101	96.3	.57	6.6	.34
M7	4.9	19.0	26.7	130	66.5	63.0	.56	4.0	.06
M2	3.2	8.9	17.3	160	34.6	42.8	.33	2.9	.01E

[a]Suspended sediment includes solids retained on a 1.5-micrometer filter.

[b]Seston includes suspended sediment and suspended fine particulates retained on a 0.7-micrometer filter.

[c]Ratio computed as suspended sediment divided by seston, expressed as percent; value larger than 100 percent displayed as 100.

[d]Particulate organic carbon computed as total organic carbon minus dissolved organic carbon; negative difference displayed as zero.

[e]Ratio computed as particulate organic carbon divided by seston, expressed as percent; zero ratio indicates zero particulate organic carbon.

[f]Ratio computed as sum of chlorophyll-a and pheophytin-a divided by seston, expressed as percent.

Table 2–4. Unfiltered total mercury and water-quality characteristics of effluent samples, Grand Calumet River/Indiana Harbor Canal, Lake County, Indiana, May 2002.

[ID, identification; ng/L, nanogram per liter; s.u., standard unit; mg/L, milligram per liter; °C, degree Celsius; µS/cm, microsiemen per centimeter; GCR, Grand Calumet River; IHC, Indiana Harbor Canal]

Sampling-location ID	and name	Unfiltered total mercury (ng/L)	pH (s.u.)	Dissolved oxygen (mg/L)	Water temperature (°C)	Specific conductance (µS/cm)
MO1	West Branch GCR municipal outfall 1	1.08[a]	7.1	9.0	16.0	678
MO2	West Branch GCR municipal outfall 2	2.48	7.2	8.2	15.5	792
IO1	IHC industrial outfall	3.71	7.7	6.6	23.5	678

[a]Concentration in one of two sequential duplicate samples.

Table 2–5. Total mercury in field-blank samples, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, May 2002.

[ID, identification; ng/L, nanogram per liter; n.a., not analyzed; -- , does not apply; < , less than reporting limit listed]

Sample ID	Unfiltered total mercury (ng/L)	Particulate total mercury (ng/L)	Total mercury in blank water (ng/L)	Blank-corrected total mercury (ng/L)	Explanation
BW1	0.09	n.a.	0.08	--	Concentration of mercury in blank water poured from field container into sample bottle was computed by subtracting mercury from preservative (0.01 ng/L)[a].
BW2	.05	n.a.	.04	--	Same as above.
BW3	.13	n.a.	.12	--	Same as above.
BW4	.13	n.a.	.12	--	Same as above.
Mean	**--**	**--**	**.09**	**--**	Mean concentration of mercury in blank water computed from four samples.
EB1	.06	n.a.	--	0	Blank-corrected concentration of mercury in unfiltered, pumped field blank was computed by subtracting mean concentration in blank water (0.09 ng/L).
EB2	.07	n.a.	--	0	Same as above.
EB3	.15	n.a.	--.	.06	Same as above.
EB4	.11	n.a.	--	.02	Same as above.
Mean	**--**	**--**	**--**	**.02**	Mean blank-corrected concentration of mercury in four field blanks.
FB1	n.a.	<.03	--	0	Blank-corrected concentration of mercury on filter was computed by subtracting mean concentration in blank water (0.09 ng/L).
FB2	n.a.	.12	--	.03	Same as above.
Mean	**--**	**--**	**--**	**.01**	Mean blank-corrected concentration of mercury in two field blanks.

[a]Maximum concentration added to blank water (0.01 nanogram per liter) was based on 0.3010-per-liter mercury remaining in acid preservative after field use, diluted at 20-milliliter acid per 500-milliliter sample.

Table 2–6. Variability of selected constituents in sequential duplicate samples, Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, May 2002.

[ID, identification; ng/L, nanogram per liter; RPD, relative percent difference]

Sampling-location ID	Unfiltered total mercury (ng/L)				Unfiltered methylmercury (ng/L)			
	First sample	Second sample	Difference[a]	RPD[b]	First sample	Second sample	Difference[a]	RPD[b]
M18	2.50	2.52	0.02	0.8	0.124	0.113	0.011	9.3
M9	45.39	49.61	4.22	8.9	.198	.197	.001	.5
M7	22.94	24.00	1.06	4.5	.075	.061	.014	20.6
IH1	.91	.92	.01	1.1	n.a.	n.a.	n.a.	n.a.
MO2	2.47	2.48	.01	.4	n.a.	n.a.	n.a.	n.a.

[a]Difference between concentration of first sample and concentration of second sample.

[b]Relative percent difference is the difference of the two concentrations divided by the average of the concentrations, expressed as percent (for comparative purposes).

Table 3–1. U.S. Geological Survey National Water Information System site-identification numbers for locations sampled in the Grand Calumet River/Indiana Harbor Canal and Lake Michigan, Lake County, Indiana, August 2001 and May 2002.

[ID, identification; USGS, U.S. Geological Survey; NWIS, National Water Information System]

Sampling-location ID and name		USGS NWIS site-identification number
M19	Grand Calumet Lagoons, west	USGS413649087171201
M18	East Branch Grand Calumet River headwaters	USGS413630087180401
M16	East Branch Grand Calumet River at Bridge St.	USGS413632087221601
M14	East Branch Grand Calumet River at Cline Ave.	USGS413647087255700
M13	East Branch Grand Calumet River at Kennedy Ave.	USGS413650087274201
M12	West Branch Grand Calumet River at Hohman Ave.	USGS5536357
M9	West Branch Grand Calumet River at Indianapolis Blvd.	USGS413651087285001
M7	Indiana Harbor Canal at Columbus Dr.	USGS413822087281601
M6	Indiana Harbor Canal at Lake George Canal	USGS413848087284201
M4	Indiana Harbor Canal at Dickey Rd.	USGS413919087273201
M2	Indiana Harbor Canal at mouth of Indiana Harbor	USGS414003087263300
IH1	Indiana Harbor near industrial intake	USGS414050087264401
LM1	Lake Michigan near industrial intake 1	USGS414009087243401
LM2	Lake Michigan near industrial intake 2	USGS413821087223001
MO1	West Branch Grand Calumet River municipal outfall 1	USGS413657087293300
MO2	West Branch Grand Calumet River municipal outfall 2	USGS413659087284701
IO1	Indiana Harbor Canal industrial outfall	USGS413858087280501

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