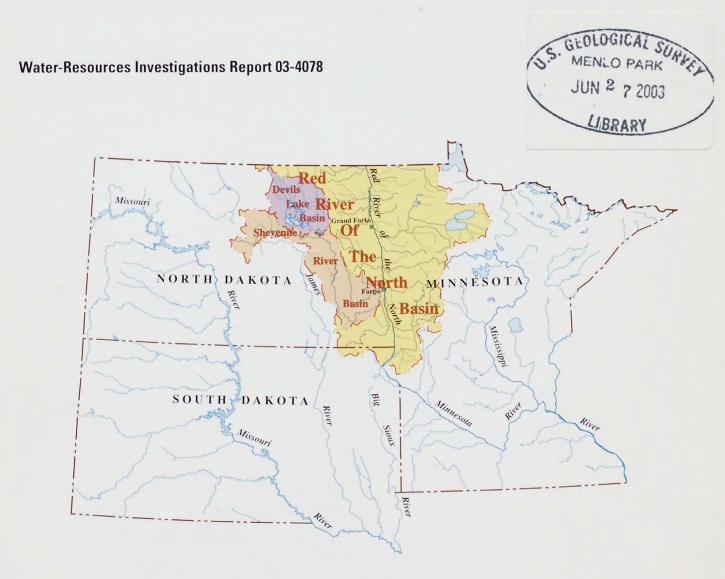


In cooperation with the U.S. Army Corps of Engineers

Reconnaissance of Mercury in Lakes, Wetlands, and Rivers in the Red River of the North Basin, North Dakota, March Through August 2001





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By Steven K. Sando, G. J. Wiche, R. F. Lundgren, and Bradley A. Sether

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In cooperation with the U.S. Army Corps of Engineers

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Abstract

Devils Lake rose dramatically during the 1990's, causing extensive flood damages. Because of the potential for continued flooding, the U.S. Army Corps of Engineers has been conducting studies to evaluate the feasibility of constructing and operating an outlet from Devils Lake. The occurrence of mercury in lakes, wetlands, and rivers and the potential for increased loading of mercury into the Sheyenne River as a result of a Devils Lake outlet needed to be evaluated as part of the studies.

Sixteen lake, wetland, and river sites in the Devils Lake, Sheyenne River, Red River of the North, and Red Lake River Basins were sampled and analyzed for mercury constituents and other selected properties and constituents relevant to mercury aquatic chemistry. For the lake and wetland sites, whole-water methylmercury concentrations ranged from less than 0.04 to 3.53 nanograms per liter and whole-water total mercury concentrations ranged from 0.38 to 7.02 nanograms per liter. Conditions favorable for methylation of mercury generally exist at the lake and wetland sites, as indicated by larger dissolved methylmercury concentrations in near-bottom samples than in near-surface samples and by relatively large ratios of methylmercury to total mercury (generally greater than 10 percent for the summer sampling period). Total mercury concentrations were larger for the summer sampling period than for the winter sampling period for all lake and wetland sites. A wetland site in the upper Devils Lake Basin had the largest mercury concentrations for the lake and wetland sites.

For the river sites, whole-water methylmercury concentrations ranged from 0.15 to 1.13 nanograms per liter and whole-water total mercury concentrations ranged from 2.00 to 26.90 nanograms per liter. Most of the mercury for the river sites occurred in particulate inorganic phase. Summer ratios of whole-water methylmercury to whole-water total mercury were 35 percent for Starkweather Coulee (a wetland-dominated site), near or less than 10 percent for the Sheyenne River sites, and less than 8 percent for the Red River of the North and Red Lake River sites.

Although the number of samples collected during this investigation is small, results indicated an outlet from Devils Lake probably would not have adverse effects on mercury concentrations in the Sheyenne River upstream from Lake Ashtabula. However, because discharges in the Sheyenne River would increase during some periods, loads of mercury entering Lake Ashtabula also would increase. Lake Ashtabula probably serves as a sink for suspended sediment and mercury. Thus, a Devils Lake outlet probably would not have substantial effects on mercury concentrations and loads in the downstream part of the Sheyenne River or in the Red River of the North. More substantial effects could occur for Lake Ashtabula.

INTRODUCTION

The Devils Lake Basin is a closed subbasin (fig. 1) within the Red River of the North Basin. At an elevation of about 1,446.5 feet above National Geodetic Vertical Datum of 1929, Devils Lake begins to spill into Stump Lake; and at an elevation of about 1,459 feet above National Geodetic Vertical Datum of 1929, the combined lakes begin to spill through Tolna Coulee into the Sheyenne River (fig. 1).



Figure 1. Location of study area and water-quality sampling sites.

Since the end of glaciation about 10,000 years ago, Devils Lake has fluctuated between spilling and being dry. Research by the North Dakota Geological Survey indicates Devils Lake has overflowed into the Sheyenne River at least twice during the past 4,000 years and has spilled into the Stump Lakes several times (Bluemle, 1991; Murphy and others, 1997). John Bluemle, North Dakota State Geologist, concluded the natural condition for Devils Lake is either rising or falling, and the lake should not be expected to remain at any elevation for a long period of time.

Recent conditions indicate the lake is in a rising phase. The lake rose more than 25 feet from February 1993 to July 2001, and flood damages in the Devils Lake Basin have exceeded \$400 million (Vecchia, 2002). Because of the potential for continued lake-level rises and the potential for additional damages, the U.S. Army Corps of Engineers, using authorities provided to the Secretary of the Army, has been conducting engineering and environmental studies to evaluate the feasibility of constructing and operating an outlet from Devils Lake. The occurrence of mercury in the Red River of the North Basin and the potential for increased loading of mercury into the Sheyenne River as a result of a constructed outlet from Devils Lake needed to be considered and evaluated as part of the studies. Therefore, the U.S. Geological Survey, in cooperation with the U.S. Army Corps of Engineers, conducted a reconnaissance investigation of mercury in lakes, wetlands, and rivers in the Red River of the North Basin. Specific objectives of the investigation were to (1) sample seven sites in the Devils Lake Basin, five sites in the Sheyenne River Basin, and four sites in the Red River of the North Basin for

mercury and selected constituents that affect the occurrence and partitioning of mercury in aquatic systems; (2) determine concentrations and masses of mercury constituents in Devils Lake and Lake Ashtabula; (3) determine concentrations and loads of mercury constituents at sites on the Sheyenne River, the Red River of the North, and the Red Lake River; (4) compare mercury data collected during this investigation with data collected during 1991-93 at various locations in the Devils Lake and Sheyenne River Basins and with data collected in other aquatic systems; and (5) relate mercury concentrations in the Devils Lake and Red River of the North Basins to the current state of knowledge concerning mercury toxicity, health effects, and effects on aquatic systems.

Mercury is a ubiquitous environmental contaminant and comes from many natural and anthropogenic sources. Typically, mercury occurs in very low concentrations in surface waters, in both inorganic and organic forms. Inorganic mercury is not particularly toxic but, under certain conditions, can be converted to organic mercury (methylmercury, a potent neurotoxin) by bacterially-mediated methylation and then assimilated by aquatic organisms and magnified in the food chain (Krabbenhoft and Rickert, 1995). Even very small amounts of inorganic mercury can cause problems in aquatic ecosystems when conditions are suitable for methylation, which primarily occurs as a byproduct of bacterially-mediated sulfate reduction. The primary conditions that are necessary for sulfate reduction (and, thus, methylation of mercury) include the presence of adequate concentrations of sulfate and organic material and a lack of dissolved oxygen (Krabbenhoft, 1996). These conditions do not have to be prevalent throughout a given aquatic ecosystem but must exist at least in isolated microzones for methylation of mercury to occur.

Methylmercury, which is produced by methylation of inorganic mercury, is a potent form of organic mercury and is among the most toxic and widespread contaminants affecting the Nation's aquatic ecosystems (Brumbaugh and others, 2001). Methylation and bioaccumulation of mercury pose toxicological risks to both fish (Wiener and Spry, 1996) and humans (U.S. Environmental Protection Agency, 1997). Because of serious concerns about methylmercury toxicity, the U.S. Environmental Protection Agency recently reduced the recommended standard for methylmercury in fish tissue from 0.5 milligram per kilogram to 0.3 milligram per kilogram (U.S. Environmental Protection Agency, accessed February 8, 2001). Methylmercury contamination also has caused many states, including North Dakota, to issue fish-consumption advisories. In North Dakota, an advisory was issued in the early 1990's when elevated mercury concentrations were detected in sport fish in Devils Lake.

This report presents the concentrations of mercury constituents for several lake, wetland, and river water-quality sampling sites; the masses of mercury in the lakes and wetlands; and the loads of mercury transported in the rivers at the times of sampling. The scope of the report is a reconnaissance-level assessment of the occurrence of mercury in the Red River of the North Basin. Data in the report can be used to assess whether the introduction of water from Devils Lake is a threat to human health and to aquatic-health systems of the Red River of the North Basin.

DESCRIPTION OF STUDY AREA

Characteristics of the Devils Lake and Red River of the North Basins have been described in detail by Wiche and Pusc (1994) and Stoner and others (1993), respectively. Much of the following information was taken from their reports.

The Devils Lake Basin is a 3,810-square-mile closed basin in northeastern North Dakota. About 3,320 square miles of the basin is tributary to Devils Lake, and the remainder is tributary to Stump Lake. The eastern, western, and northern boundaries of the Devils Lake Basin are poorly defined low divides. The southern boundary is a series of recessional moraines that lie between Devils Lake and the Sheyenne River.

The Red River of the North originates at the confluence of the Otter Tail and Bois de Sioux Rivers on the border between North Dakota and Minnesota and then flows about 394 miles northward into Manitoba, Canada. The Red River of the North has a drainage area of about 40,200 square miles near the Canadian border. Most tributaries to the Red River of the North enter from the east, but the Sheyenne River, which constitutes a relatively large tributary, enters the Red River of the North from the west. The Sheyenne River has a contributing drainage area of about 3,090 square miles, which is about 8 percent of the drainage area of the Red River of the North at the Canadian border. Mean annual flow for the Sheyenne River is about 5 percent of mean annual flow at the border. The Red Lake River, another large tributary to the Red River of the North, enters the Red River of the North from the east at East Grand Forks. The Red Lake River has a drainage area of about 5,970 square miles, which is about 15 percent of the drainage area of the Red River of the North at the Canadian

border. Mean annual flow for the Red Lake River is about 30 percent of mean annual flow at the border. The slope of the Red River of the North ranges from about 1.3 feet per mile near the headwaters to about 0.2 foot per mile at the Canadian border. The river meanders are mature, and the streambed is comprised mostly of clay- and silt-sized particles.

The climate of the Red River of the North Basin is continental and ranges from dry subhumid in the western part of the basin to subhumid in the eastern part of the basin. The basin has cold winters and moderately warm summers. According to the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Environmental Data Service (1982), mean annual temperatures range from 37 to 43°F, and mean monthly temperatures range from -1°F in January in the northern part of the basin to 73°F in July in the southern part of the basin. Mean annual precipitation ranges from about 17 inches in the western part of the basin to about 26 inches in the eastern part of the basin. About three-fourths of the annual precipitation falls from April through September. Mean annual net evaporation ranges from about 4 inches in the eastern part of the basin to about 22 inches in the western part of the basin. Climatic characteristics of the Devils Lake Basin are very similar to those in the western part of the Red River of the North Basin.

Geologic and topographic features of both the Devils Lake and Red River of the North Basins primarily are a result of depositional and erosional effects of continental glaciation. Surficial geology consists of a thick mantle of glacial drift (consisting of till and outwash) that is 150 to 300 feet thick in the Red River of the North Basin. Upland areas are dominated by till that is composed mostly of clay and silt. Cretaceous-age marine sediments underlie the glacial drift in most areas. Effects of glaciation in both the Devils Lake and Red River of the North Basins are indicated by the numerous shallow depressions and potholes in the basins.

METHODS OF STUDY

Water samples were collected at 16 sites (table 1), including 1 wetland site in the upper Devils Lake Basin, 1 site on Starkweather Coulee, 5 sites on Devils Lake, 3 sites on the Sheyenne River, 2 sites on Lake Ashtabula, 3 sites on the Red River of the North, and 1 site on the Red Lake River. The water samples collected at these sites were analyzed for the selected properties and constituents given in table 2.

Table 1. Water-quality sampling sites

[--, not determined]

Site number (see figure 1 for location)	Site name	Site identification number	Drainage area (square miles
1	Wetland site in upper Devils Lake Basin	482818098463800	
2	Starkweather Coulee near Webster, North Dakota	05056239	310
3	Devils Lake West Bay near Pelican Lake	480818099100000	
4	Devils Lake West Bay southwest	480306099140000	
5	Devils Lake Main Bay	480147098572200	
6	Devils Lake East Bay	480050098454100	
7	East Devils Lake	475740098381600	
8	Sheyenne River near Warwick, North Dakota	05056000	2,070
9	Lake Ashtabula near north end	471256097573900	
10	Lake Ashtabula at Baldhill Dam, North Dakota	05057500	7,470
11	Sheyenne River below Baldhill Dam, North Dakota	05058000	7,470
12	Sheyenne River near Kindred, North Dakota	05059000	8,800
13	Red River of the North at Fargo, North Dakota	05054000	6,800
14	Red River of the North at Halstad, Minnesota	05064500	21,800
15	Red Lake River at Fisher, Minnesota	05080000	5,678
16	Red River of the North at Emerson, Manitoba	05102500	40,200

Property or constituent	Reporting level used in investigation
FIEI	LD ANALYSES
	properties and constituents
(U.S. Geological St	urvey North Dakota District)
Specific conductance	10 microsiemens per centimeter
pH	0.1 standard unit
Water temperature	0.1 degree Celsius
Dissolved oxygen	0.1 milligram per liter
LABORA	TORY ANALYSES
9	ted trace-element constituents artment of Health Laboratory)
Calcium, dissolved	0.1 milligram per liter
Magnesium, dissolved	0.1 milligram per liter
Sodium, dissolved	0.1 milligram per liter
Potassium, dissolved	0.1 milligram per liter
Alkalinity, dissolved	0.1 milligram per liter
Sulfate, dissolved	0.1 milligram per liter
Chloride, dissolved	0.1 milligram per liter
Iron, whole water	10 micrograms per liter
Manganese, whole water	10 micrograms per liter
	sediment constituents
(U.S. Geological Survey I	owa District Sediment Laboratory)
Suspended sediment	1 milligram per liter
Suspended sediment (finer than 0.062 millimeter)	1 percent
	ury constituents
	sconsin District Mercury Laboratory)
Methylmercury, dissolved	0.04 nanogram per liter
Methylmercury, particulate	0.02 nanogram per liter
Methylmercury, whole water	0.04 nanogram per liter
Total mercury, dissolved	0.04 nanogram per liter
Total mercury, particulate	0.02 nanogram per liter
Total mercury, whole water	0.04 nanogram per liter
	carbon constituents sconsin District Mercury Laboratory)
Organic carbon, dissolved	0.1 milligram per liter
One and a second	() 1 :11: :1:t

Organic carbon, dissolved	0.1 milligram per liter
Organic carbon, whole water	0.1 milligram per liter

Sample Collection, Processing, and Analysis

Sampling for mercury in the natural environment poses many problems. Although mercury typically occurs in extremely low concentrations in water, it also may be present in very low but problematic concentrations in the ambient atmosphere (either in gaseous form or within airborne particles) and on surfaces near or in the sampling and processing environment. Thus, extreme precautions are necessary during sample collection, and exposure of the water sample to different collection/processing containers (or the ambient atmosphere) must be kept to a minimum. For this investigation, two-person ultra-clean sampling procedures ("clean hands/dirty hands"; U.S. Environmental Protection Agency, 1996; Olson and DeWild, 1999) were used to collect the water samples analyzed for mercury constituents. The collectors wore clean TYVEK suits, shoulder-length polyethylene gloves, and wrist-length latex gloves. Sample bottles were contained within double polyethylene bags. Any materials and containers that contacted the sample water were rigorously cleaned using procedures described by Olson and DeWild (1999), the U.S. Environmental Protection Agency (2001), and DeWild and others (2002).

Lake and wetland sites were sampled once in mid-March during ice cover and inverse thermal stratification and once in late summer during peak heating conditions. Sampling periods were selected to represent conditions most conducive for the occurrence of methylmercury in lacustrine settings. In northern temperate lakes, large amounts of methylmercury typically can be generated during winter stratification under ice (David Krabbenhoft, U.S. Geological Survey, oral commun., 2000), primarily because the stratification is particularly stable and results in an extended period of near-sediment oxygen depletion. Although microbial metabolic rates are slowed in winter, conditions suitable for sulfate reduction can continue for a long duration and can result in accumulation of methylmercury. During peak heating conditions in late summer, wind-generated turbulence can disrupt thermal stratification in northern prairie lakes, and stratification might not be as stable as during winter. However, microbial metabolic rates are high and available oxygen can be consumed quickly in the process of breaking down organic material. Also, during calm periods, near-sediment oxygen depletion can occur quickly, promoting sulfate reduction and accumulation of methylmercury.

Lake samples were collected through ice during the winter sampling trip and from a boat during the summer sampling trip. During the winter sampling trip, a hole was drilled in the ice, upwind from any vehicles, using a pre-cleaned manual steel auger. Several gallons of native lake water then were purged from the hole before sample collection. Vertical profiles of field-measured properties and constituents (table 2) were made during each sampling trip. All lake samples were collected using a rigorously cleaned peristaltic pump with Teflon tubing. Near-surface samples (taken about 3 feet below the water surface) were collected at all sites during both sampling trips, and near-sediment samples (taken about 3 feet above the lake bottom) were collected at four sites (sites 3, 5, 7, and 10) during both sampling trips.

Because the wetland site was inaccessible during the winter sampling trip, the first wetland sample was not collected until after ice out. The second wetland sample was collected in late summer at about the same time that lake samples were collected. The wetland sample was collected by wading to a point near the center of the wetland and using a rigorously cleaned 1-liter Teflon bottle to obtain a grab sample.

River sites were sampled once in late April/early May during spring-runoff conditions and once in late summer during low-flow/peak heating conditions. Because little is known about seasonal variability of mercury constituents in northern prairie streams, sampling periods were selected to represent a wide range of flow and environmental conditions.

River samples were collected from a boat near the centroid of flow in the stream cross section, and field properties and constituents (table 2) were measured at mid-depth near the centroid of flow. Because water samples analyzed for mercury are susceptible to contamination, depth- and width-integrating procedures that require the transfer of a sample to multiple containers in the field generally are not recommended for low-level mercury analysis. Also, flowing-water conditions are problematic when using ultra-clean sampling procedures with a peristaltic pump. Thus, river samples were collected from just below the water surface using rigorously cleaned 1-liter Teflon bottles to obtain grab samples. To minimize exposure to the ambient atmosphere, collection bottles were submersed while capped, then uncapped and filled, and then recapped while still submersed. For all sampling sites, water samples were collected for analysis of mercury constituents and then for analysis of major-ion, trace-element, suspended-sediment, and organic-carbon samples were collected using equipment and techniques that were similar to those used for mercury samples. However, some of the extreme precautions, such as rigorous acid cleaning and double bagging of sample bottles, that were necessary for collection of mercury samples were not used for collection of major-ion, trace-element, suspended-sediment, and organic-carbon samples. Because those constituents occur in much greater concentrations than mercury, the potential for contamination is much less than for mercury.

Water samples were processed and analyzed for major-ion and selected trace-element constituents by the North Dakota Department of Health Laboratory (NDDHL). To determine dissolved concentrations of major-ion constituents, water samples were passed through 0.45-micrometer pore-size filters. Thus, in this report, for major-ion constituents, "dissolved" is operationally defined as that part of a water sample that passes through a 0.45-micrometer filter. To determine whole-water concentrations of trace-element constituents, water samples were not filtered before analysis and, thus, included both dissolved and particulate phases. Quality-assurance and analytical procedures are described in the NDDHL environmental methods handbook (North Dakota Department of Health, 2001).

Water samples were processed and analyzed for suspended-sediment constituents by the U.S. Geological Survey Iowa District Sediment Laboratory. Analytical and quality-assurance procedures are described by Guy (1969) and Matthes and others (1991).

Water samples were processed and analyzed for mercury and organic-carbon constituents by the U.S. Geological Survey Wisconsin District Mercury Laboratory (WDML), a class-100, clean-room facility. WDML quality-assurance procedures (Wisconsin District Mercury Laboratory, 1999) are available at URL http://infotrek.er.usgs.gov/doc/mercury/ qa.html (accessed March 6, 2002). Water samples were analyzed at the WDML for determination of methylmercury (Olson and DeWild, 1997c, 1997d) and total mercury (Olson and DeWild, 1997a). In this report, the term "total" with respect to mercury refers to both the inorganic and organic forms combined. Analyses for organic-carbon constituents were performed using procedures described by Olson and DeWild (1997b). To determine dissolved concentrations of mercury and organic-carbon constituents, water samples were passed through ultra-clean, 0.7-nominal-pore-size, quartzfiber filters at the WDML within 24 hours of sample collection. Thus, in this report, for mercury and organic-carbon constituents, "dissolved" is operationally defined as that part of a water sample that passes through a 0.7-micrometer filter. To determine particulate concentrations of mercury constituents, known volumes of sample water were passed through ultra-clean, 0.7-nominal-pore-size, quartz-fiber filters. The filter and retained particulate material were digested and the resulting solution was analyzed. Mass/volume concentrations of particulate mercury constituents then were determined on the basis of the original known volume of sample water filtered. To determine whole-water concentrations of mercury constituents, dissolved and particulate concentrations were summed. If either the dissolved or particulate concentration for a given sample was less than the reporting level, the concentration for the "less-than" fraction was assumed to be zero.

Quality Assurance/Quality Control

Quality-assurance/quality-control samples were collected to assess precision and accuracy of collected data. One field-equipment blank sample and one replicate sample were collected during each sampling trip and analyzed for mercury and organic-carbon constituents. Fewer quality-assurance/quality-control samples were collected for major-ion and trace-element constituents because those constituents are not as susceptible to contamination as mercury constituents. For major-ion and trace-element constituents, one replicate sample was collected during the first lake-sampling trip and another was collected during the first river-sampling trip. Blank samples were collected by passing ultra-clean water through the collection and processing equipment used for primary environmental samples. Replicate samples were collected and processed, and procedures used for replicate samples were identical to those used for primary environmental samples.

Estimation of Masses and Loads

Coarse estimates of masses of mercury constituents for lake and wetland sites were calculated to investigate the processing and fate of mercury in lakes and wetlands. Masses were estimated by multiplying lake and wetland volumes by representative constituent concentrations and by a conversion factor (0.00123) to convert the sample concentration (in milligrams per liter) to the total mass of the constituent in the given water body (in grams).

Volumes for the Devils Lake sites were estimated using records of the Devils Lake water-surface elevation at U.S. Geological Survey gaging station 05056500 (Devils Lake near Devils Lake, N. Dak.) and elevation/capacity curves for Devils Lake (Aldo V. Vecchia, U.S. Geological Survey, written commun., March 27, 2002). Volumes for the Lake Ashtabula sites were estimated using records of water-surface elevation and elevation/capacity curves provided by the U.S. Army Corps of Engineers (U.S. Army Corps of Engineers, 2002). The volume for the wetland site was estimated using a visual estimate of surface area and the average depth of the wetland at the time of sampling.

Representative constituent concentrations were determined using the following guidelines. For lake and wetland sites where only one sample in the vertical was collected (that is, for sites 1, 4, 6, and 9 where only a near-surface sample was collected), constituent concentrations in that sample were assumed to represent constituent concentrations in the entire water body represented by the sampling site. For example, for site 6 (Devils Lake East Bay), a single near-surface sample was collected during each sampling trip. Constituent concentrations in that sample were assumed to represent constituent concentrations in the entire water volume for Devils Lake East Bay for the sampling period. For lake and wetland sites where two samples in the vertical were collected (that is, for sites 3, 5, 7, and 10 where near-surface and near-bottom samples were collected), the proportion of the water column represented by each of the two samples was estimated by inspecting the vertical profiles of field-measured properties and constituents. For example, for the winter sampling at site 5 (Devils Lake Main Bay), field measurements of specific conductance, water temperature, and dissolved oxygen

(supplement 1) indicate that the hypolimnion (where more reducing conditions would be expected to occur) existed from about 39 to 46 feet below the water surface. That depth represented about 14 percent of the total water column. Thus, to determine representative constituent concentrations for site 5, the near-bottom sample constituent concentrations were multiplied by 0.14, and the near-surface sample constituent concentrations were multiplied by 0.86. The two concentrations then were summed to obtain vertically-weighted constituent concentrations for that site. The vertically-weighted constituent concentrations in the entire water volume for Devils Lake Main Bay for the sampling period. For samples in which constituent concentrations were less than the reporting level, representative constituent concentrations were assumed to be zero.

Masses of mercury constituents for Devils Lake were estimated by summing masses for individual bays. Masses of mercury constituents for Lake Ashtabula were estimated by summing masses for the two sampling sites on Lake Ashtabula. Site 9 (Lake Ashtabula near north end) was assumed to represent 20 percent of the entire water volume for Lake Ashtabula, and site 10 (Lake Ashtabula at Baldhill Dam, N. Dak.) was assumed to represent 80 percent of the entire water volume for Lake Ashtabula.

Loads of mercury constituents for river sites were estimated by multiplying stream discharges at the times of sampling by representative constituent concentrations and by a conversion factor (0.00245) to convert cubic feet per second and nanograms per liter to grams per day. A single near-surface grab sample was collected for each river site, and constituent concentrations in that sample were assumed to represent constituent concentrations in the entire water volume flowing past the site at the time of sampling.

Mass estimates in this report should be considered coarse. The relatively small number of samples collected during the investigation may not accurately represent spatial variability of mercury constituents in the water bodies, and errors in volume estimates for the water bodies and analytical errors also may exist. However, for this reconnaissance-level assessment of the occurrence of mercury in the Red River of the North Basin, the methods used to estimate the masses probably are reasonable for assessing relative differences between different water bodies and between different sampling periods. In addition, the near-surface grab sample collected for each river site may not accurately represent the vertical and horizontal variability of mercury constituents in the rivers, and errors associated with discharge estimates and analytical errors also may exist. However, load estimates for the river sites probably are reasonable and adequate for discerning differences between sites and between different sampling periods.

RESULTS FOR QUALITY-ASSURANCE/QUALITY-CONTROL SAMPLES AND FOR SELECTED PROPERTIES AND CONSTITUENTS

Field and analytical data collected during this investigation are given in supplements 1 through 6 at the back of the report. Results for field-measured properties and constituents are given in supplement 1 for lake and wetland sites and in supplement 2 for river sites. Laboratory analytical results for major-ion and selected trace-element constituents are given in supplement 3 for lake and wetland sites and in supplement 4 for river sites, and laboratory analytical results for organic-carbon constituents are given in supplement 5 for lake and wetland sites and in supplement 6 for river sites.

Quality-Assurance/Quality-Control Samples

Concentrations of mercury and organic-carbon constituents in field-equipment blank samples (table 3) generally were less than the reporting level and were substantially less than typical concentrations in the environmental samples (supplements 5 and 6). A comparison of results for the primary environmental samples and the replicate samples generally indicates good agreement (tables 4 and 5). A typical data-quality objective for the precision of replicate samples is a relative percent difference (RPD) less than or equal to 20 percent (Taylor, 1987). Nearly all values for the replicate samples had RPD values that met this criterion. However, one dissolved total mercury concentration and one dissolved chloride concentration substantially exceeded the criterion, and one dissolved methylmercury concentration and one particulate total mercury concentration slightly exceeded the criterion. Generally, problems in the quality-assurance/ quality-control data were few and probably did not interfere with evaluation of the data.

Table 3. Concentrations of mercury and organic-carbon constituents in quality-assurance/quality-control field-equipment blank samples [ng/L, nanograms per liter; mg/L, milligrams per liter; <, less than; ND, not determined]

Site number (see figure 1 for location)	Site where blank was collected	Date	Time	Methyl- mercury, dissolved (ng/L)	Methyl- mercury, particulate (ng/L)	Total mercury, dissolved (ng/L)	Total mercury, particulate (ng/L)	Organic carbon, dissolved (mg/L)	Organic carbon, whole water (mg/L)
7	East Devils Lake	03/14/01	1655	< 0.04	ND	0.20	< 0.02	ND	ND
7	East Devils Lake	08/02/01	0950	<.04	< 0.02	.20	<.02	0.1	0.1
15	Red Lake River at Fisher, Minnesota	07/25/01	1340	<.04	<.02	.30	.30	<.1	<.1
16	Red River of the North at Emerson, Manitoba	05/02/01	0735	<.04	<.02	.10	<.02	<.1	ND

Field-Measured Properties and Constituents

Vertical profiles of field-measured properties and constituents for lake and wetland sites (supplement 1) provide information about general water-quality conditions and about the strength of thermal stratification. Thermal stratification in lakes can be important to mercury chemistry because near-sediment oxygen depletion promotes sulfate reduction and accumulation of methylmercury. Generally, the lake and wetland sites tended to be moderately alkaline (field-measured pH values were between 6.8 and 8.7 standard units) and of relatively high ionic strength (field-measured specific-conductance values were between 1,010 and 6,930 microsiemens per centimeter). Deep lake sites (represented by site 5, Devils Lake Main Bay, fig. 2) generally showed relatively strong thermal stratification during both winter and summer sampling periods. Field-measured properties at deep sites were typical of stratified conditions (fig. 2); specific conductance increased near the bottom, and pH and dissolved oxygen decreased near the bottom. Shallow lake sites (represented by site 4, Devils Lake West Bay southwest, fig. 3) did not show strong thermal stratification in either sampling period, and field-measured properties tended to be similar at different depths.

Values for field-measured properties and constituents for river sites (supplement 2) were fairly typical of large streams in the northern Great Plains and were similar to previously reported data for the Red River of the North Basin (Stoner and others, 1998). The river sites tended to be moderately alkaline (field-measured pH values were between 7.6 and 8.4 standard units) and of moderate ionic strength (field-measured specific-conductance values were between 341 and 1,260 microsiemens per centimeter). Dissolved-oxygen concentrations generally were near saturation during spring-runoff conditions and no more than moderately depleted (percent saturation greater than about 75 percent) during the summer sampling period.

Major-Ion, Trace-Element, and Suspended-Sediment Constituents

Average dissolved-solids concentrations and ionic proportions for all sites are shown in figure 4. For the lake and wetland sites in the Devils Lake Basin (sites 1 and 3 through 7), sodium and sulfate were dominant among the cations and anions, respectively (fig. 4). Dissolved-solids concentrations and the dominance of those two ions generally increased downstream through the Devils Lake system. For the Lake Ashtabula sites (sites 9 and 10), sodium, magnesium, and calcium were about equal in dominance among the cations, and bicarbonate was slightly dominant among the anions. However, sulfate concentrations still were relatively large and exceeded 200 milligrams per liter (supplement 3). Sulfate concentrations are particularly important in mercury chemistry because methylation of mercury occurs as a byproduct of sulfate reduction. Very high rates of sulfate reduction can result in an accumulation of sulfide (the end product of sulfate reduction), which can strongly bind available mercury ions and make them unavailable for methylation of mercury. Thus, although sulfate concentrations must be greater than about 2 milligrams per liter for sulfate reduction to occur (Gilmour and Krabbenhoft, 2001), relatively large sulfate concentrations (greater than about 50 milligrams per liter; U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service, 1996) can at times provide accumulation of sulfide and inhibit methylation of mercury. For this investigation, sulfate concentrations for the lake and

0

Table 4. Analytical results for primary environmental samples and for quality-assurance/quality-control replicate samples for major-ion and trace-element constituents [μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; RPD, relative percent difference; μg/L, micrograms per liter; --, no data]

Site number (see figure 1 for location)	Site name	D. c.	Time		Specific conductance $(\mu \text{S/cm})$			Calcium, dissolved (mg/L)			Magnesium, dissolved (mg/L)		
		Date	Primary	Replicate	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	1205	1,970	1,970	0	100	110	9.5	84	90	6.9
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	0740	539	536	-0.6	56	56	0	25	24	-4.1

Site number (see figure 1 for location)	Site name	Date	Т	ime	Sodium, dissolved (mg/L)			Potassium, dissolved (mg/L)			Alkalinity, dissolved (mg/L as CaCO ₃)		
		Date	Primary	Replicate	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	1205	240	260	8.0	38	42	10.0	390	400	2.5
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	0740	18	18	0	8.2	7.9	-3.7	150	150	0

Site number (see figure 1 for location)	Site name	Site name	Site name	Site name	Date	Т	īme	Sulfate, dissolved (mg/L)		ved	С	hloride, dissol (mg/L)	ved	Solids, dissolved, sum of constituents (mg/L)		
			Primary	Replicate	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)			
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	1205	520	520	0	87	94	7.7	1,300	1,360	4.5			
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	0740	110	110	0	12	0.4	-187.1	317	308	-2.9			

Site number	Site name	Date	Т	īme	li	ron, whole wa (μg/L)	ter	Manganese, whole water $(\mu g/L)$			
(see figure 1 for location)			Primary	Replicate	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	1205	20	20	0	410	410	0	
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	0740		3,800		-	130		

Table 5. Analytical results for primary environmental samples and for quality-assurance/quality-control replicate samples for mercury and organic-carbon constituents [ng/L, nanograms per liter; RPD, relative percent difference; <, less than; mg/L, milligrams per liter]

Site number (see figure 1	Site name	Date	Time		Methylmercury, dissolved (ng/L)			Methylmercury, particulate (ng/L)			Total mercury, dissolved (ng/L)		
for location)			Primary	Replicate	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	1205	< 0.04	< 0.04	0	< 0.02	< 0.02	0	0.50	1.43	96.4
6	Devils Lake East Bay	08/02/01	0740	0750	.10	.13	26.3	.10	.09	10.5	.85	.97	13.2
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	0740	.06	.07	15.4	.10	.09	10.5	1.91	1.78	7.0
16	Red River of the North at Emerson, Manitoba	07/26/01	0715	0725	.06	.07	15.4	.31	.34	9.2	1.13	1.06	6.4

Site number (see figure 1 for location)	Site name	Site name	Date	Time		Total mercury, particulate (ng/L)			Organic carbon, dissolved (mg/L)			Organic carbon, whole water (mg/L)		
			Primary	Replicate	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	Primary	Replicate	RPD (percent)	
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	1205	< 0.02	< 0.02	0	20.72	20.69	0.1	20.99	21.18	0.9	
6	Devils Lake East Bay	08/02/01	0740	0750	.34	.45	27.8	19.22	20.02	4.1	19.57	19.84	1.4	
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	0740	7.49	7.31	2.4	8.53	8.92	4.5	8.37	8.79	4.9	
16	Red River of the North at Emerson, Manitoba	07/26/01	0715	0725	21.30	22.49	5.4	9.44	9.42	0.2	9.42	9.30	1.3	

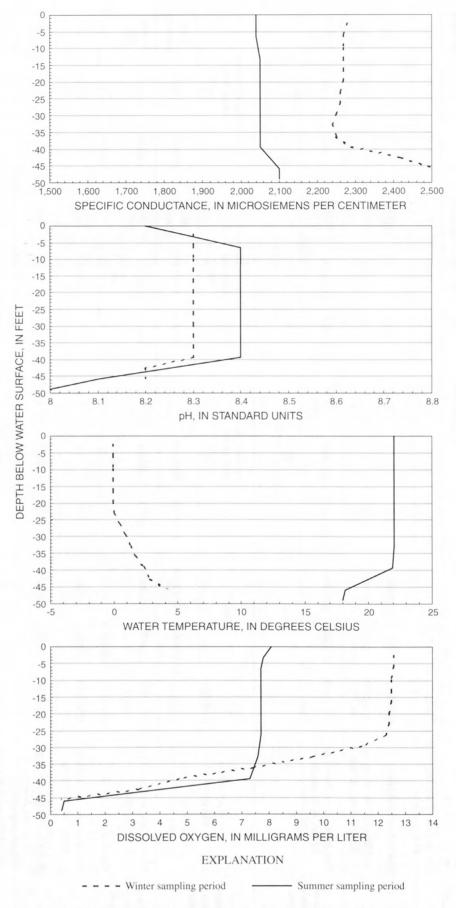


Figure 2. Vertical profiles of field-measured properties and constituents at a representative deep lake site (site 5, Devils Lake Main Bay).

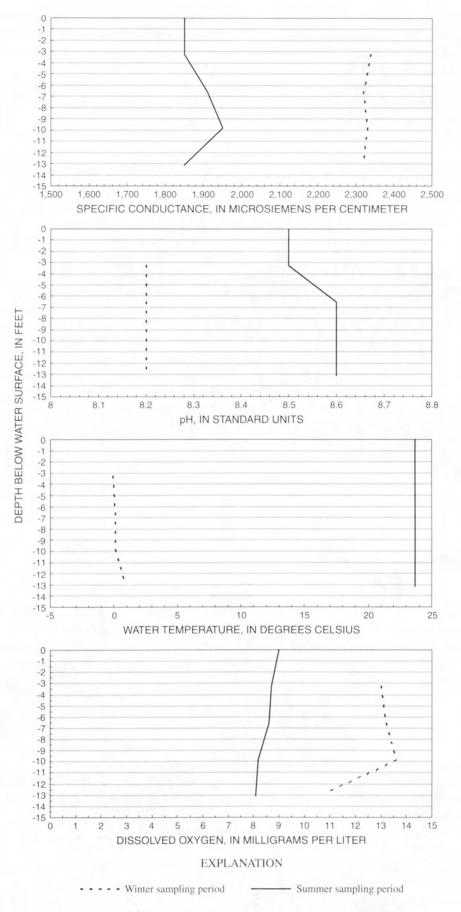


Figure 3. Vertical profiles of field-measured properties and constituents at a representative shallow lake site (site 4, Devils Lake West Bay southwest).

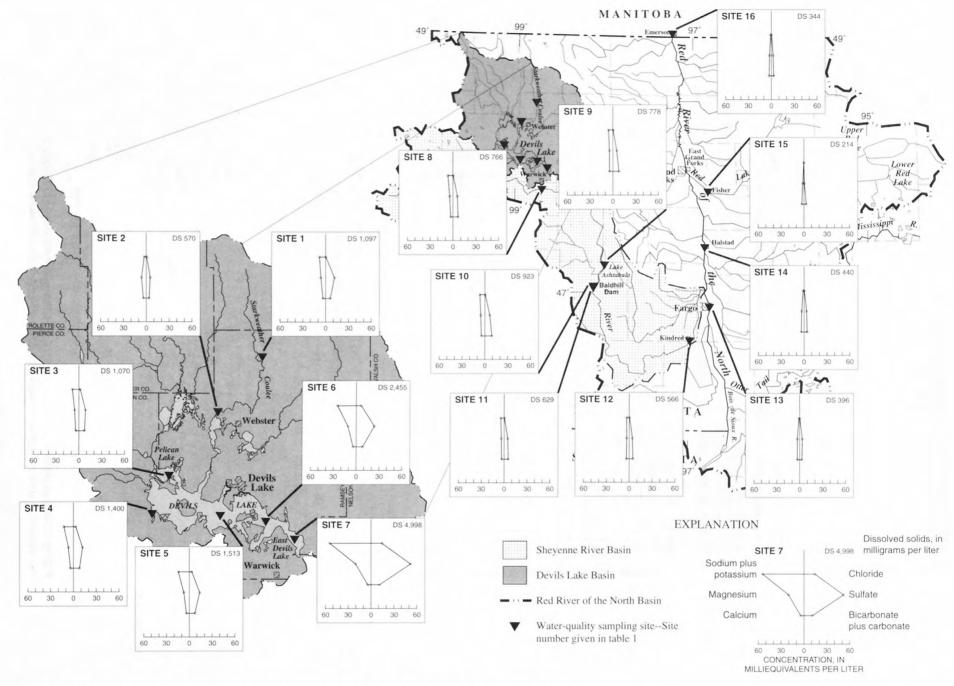


Figure 4. Average dissolved-solids concentrations and ionic proportions for water-quality sampling sites.

wetland sites were much larger than the minimum concentration required for sulfate reduction and also were much larger than concentrations reported to inhibit methylation of mercury. However, the ability of sulfide to bind with available mercury ions also can depend on several other factors, including (1) the presence of either dissolved or particulate iron and manganese, which have a strong affinity for sulfide (U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service, 1996); and (2) the presence of certain organic acids, which decrease mercury binding by sulfide (Ravichandran and others, 1999). The biological and chemical interactions that affect sulfate reduction, availability of mercury for methylation, and the inhibitory effects of sulfide on methylation of mercury are complex and site specific.

Iron and manganese concentrations for the lake and wetland sites (supplement 3) were within typical ranges for northern temperate lakes (Livingstone, 1963). The whole-water concentrations shown represent both dissolved and particulate phases of the constituents because the water samples analyzed for the constituents were not filtered. However, most of the iron and manganese probably was in dissolved phase as indicated by the small (generally less than 30 milligrams per liter; supplement 3) suspended-sediment concentrations. Near-bottom concentrations generally were larger than near-surface concentrations, especially for manganese, indicating the occurrence of iron and manganese in natural waters is sensitive to oxidation-reduction conditions. Reducing conditions near the bottom probably result in release of adsorbed ions from oxide-surface sites on inorganic sediment particles and from organic material.

For the Sheyenne River sites (sites 8, 11, and 12), sodium, magnesium, and calcium were about equal in dominance among the cations, and sulfate and bicarbonate were about equal in dominance among the anions (fig. 4). Dissolved-solids concentrations decreased slightly in a downstream direction. For the Red River of the North and Red Lake River sites (sites 13 through 16), magnesium and calcium were about equal in dominance among the cations for sites 13 and 14. Magnesium decreased in proportion in a downstream direction, and calcium became dominant among the cations for sites 15 and 16. Sulfate and bicarbonate were about equal in dominance among the anions at sites 13, 14, and 16, and bicarbonate was dominant among the anions at site 15. Dissolved-solids concentrations generally decreased in a downstream direction. Sulfate concentrations for the river sites ranged from about 15 to 290 milligrams per liter (supplement 4) and were much larger than the minimum concentration required for sulfate reduction and generally larger than the concentrations reported to inhibit methylation of mercury. However, as previously noted, the biological and chemical interactions that affect sulfate reduction and the inhibitory effects of sulfide on methylation of mercury are complex and site specific.

Whole-water iron and manganese concentrations for the river sites (supplement 4) were within previously reported ranges for sites in the Red River of the North Basin (Britton and others, 1983). Much of the iron and manganese probably was in particulate phase.

River sites tended to be fairly oxic and had moderate suspended-sediment concentrations (supplement 4). Suspended-sediment concentrations were within typical ranges for rivers in the Red River of the North Basin (Tornes and others, 1997) and were largely dependent on discharge at the time of sampling. For sites in the upper part of the Sheyenne River Basin (sites 8 and 11) (fig. 5), concentrations were small relative to the other river sites during both sampling periods. The concentrations decreased between sites 8 and 11, probably indicating that Lake Ashtabula serves as a sediment sink.

Organic-Carbon Constituents

Most of the organic carbon in water samples from the lake and wetland sites was in dissolved phase. Dissolved organic-carbon concentrations for the wetland site (site 1) ranged from about 20 to 30 milligrams per liter (supplement 5; fig. 6). For the Devils Lake sites (sites 3 through 7), concentrations ranged from about 15 to 30 milligrams per liter and had a median of about 20 milligrams per liter. For the Lake Ashtabula sites (sites 9 and 10), concentrations ranged from about 10 to 20 milligrams per liter and had a median of about 15 milligrams per liter. These concentrations generally were within typical ranges for water bodies in the Red River of the North Basin (Tornes and others, 1997; Brigham and others, 1999). Organic-carbon concentrations in water bodies in the Red River of the North tend to be larger than general concentrations for water bodies across the United States (Britton and others, 1983), indicating that waters in the Red River of the North probably have relatively high biological productivity. For this investigation, near-surface sample concentrations were similar to near-bottom sample concentrations (fig. 6). Generally, concentrations decreased slightly between winter and summer sampling periods, but for sites 1 and 9, concentrations increased slightly between sampling periods.

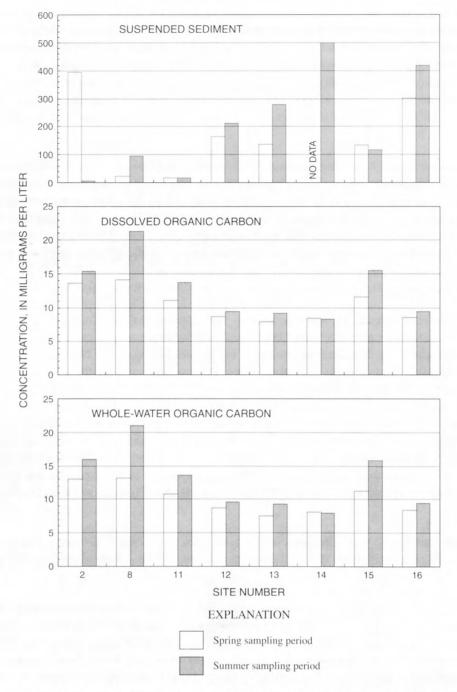


Figure 5. Concentrations of suspended sediment and organic carbon for river sites.

Most of the organic carbon in water samples from the river sites was in dissolved phase, and concentrations increased slightly between the spring and summer sampling periods (supplement 6; fig. 5). Organic-carbon concentrations generally were within typical ranges for rivers in the Red River of the North Basin (Tornes and others, 1997; Brigham and others, 1999).

MERCURY CONSTITUENTS IN LAKES, WETLANDS, AND RIVERS

In this section, mercury concentrations, masses, and loads from the reconnaissance-level sampling of lakes, wetlands, and rivers are presented and discussed. Results of the study are used to postulate possible effects from a Devils Lake outlet on mercury occurrence.

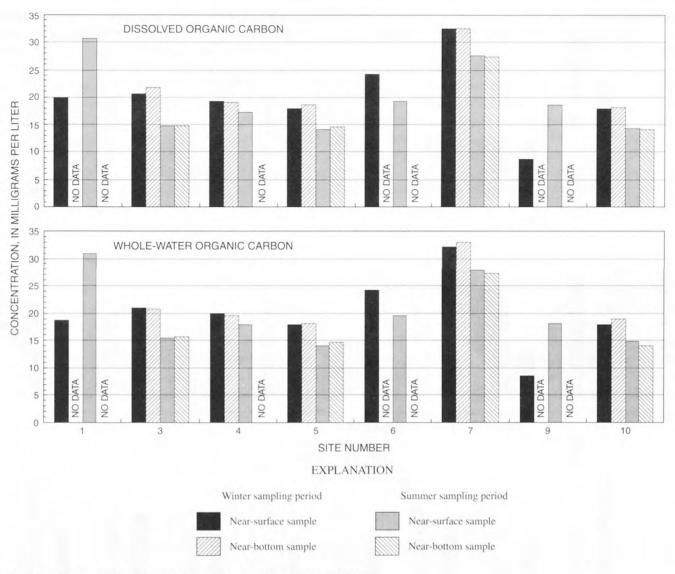


Figure 6. Concentrations of organic carbon for lake and wetland sites.

Lakes and Wetlands

Whole-water methylmercury concentrations in water samples from the lake and wetland sites ranged from 0.39 to 3.53 nanograms per liter for the wetland site (site 1), from less than 0.04 to 0.34 nanogram per liter for the Devils Lake sites (sites 3 through 7), and from less than 0.04 to 0.46 nanogram per liter for the Lake Ashtabula sites (sites 9 and 10) (supplement 5; fig. 7). Most of the sites had methylmercury concentrations that exceeded 0.10 nanogram per liter, which might be considered the upper end of the range of typical aquatic concentrations throughout the United States (Krabbenhoft and others, 1999). However, the concentrations generally were within typical ranges for natural lakes in the Red River of the North Basin in Minnesota (Brigham and others, 1999; Brigham and others, 2002) except for the largest concentration for the wetland site (site 1). That concentration (3.53 nanograms per liter) is near the largest reported concentration in the Red River of the North Basin.

For the winter sampling period, most of the methylmercury in water samples from the lake and wetland sites was in dissolved phase, and concentrations generally were less than the reporting level of 0.04 nanogram per liter (supplement 5; fig. 7). However, concentrations at sites 1, 3, and 10 were moderately large. For the summer sampling period, methylmercury concentrations (fig. 7) generally were greater than for the winter sampling period. The whole-water methylmercury concentration (3.53 nanograms per liter) for the wetland site (site 1) was large, and the concentrations for the remaining sites were moderately large. Wetlands have been reported to be favorable sites for production of

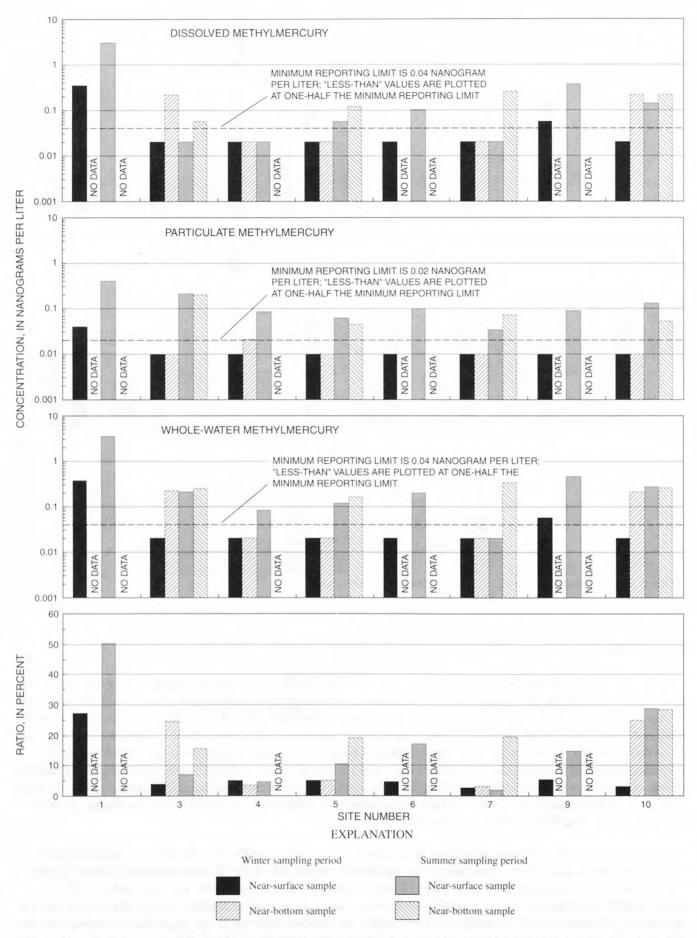


Figure 7. Concentrations of methylmercury and ratios of whole-water methylmercury to whole-water total mercury for lake and wetland sites.

methylmercury (St. Louis and others, 1994; Hurley and others, 1995). The pattern of larger methylmercury concentrations in summer than in winter differs from the seasonal pattern reported by Brigham and others (2002) for lakes and impoundments in the Red River of the North Basin in Minnesota. In Brigham's study, seasonal patterns of methylmercury were characterized by concentrations that were largest in winter, smallest in spring and fall, and intermediate in summer. However, Brigham and others (2002) showed a summer maximum for a single hypereutrophic lake, possibly indicating that seasonal patterns of methylmercury are dependent on trophic status. The lakes and wetland sampled for this investigation are hypereutrophic, which may account for the difference in the patterns of methylmercury. Dissolved methylmercury concentrations generally were larger than particulate methylmercury concentrations, probably because of larger amounts of suspended particulate organic and inorganic materials that adsorb mercury during summer. The summer particulate methylmercury concentrations at site 3 were much larger than the dissolved concentrations, possibly indicating that most of the methylmercury at site 3 is adsorbed to particulate material. Generally, near-bottom samples had larger dissolved methylmercury concentrations than near-surface samples for both sampling periods, possibly indicating production of methylmercury by sulfate reduction at the sediment-water interface and/or photodegradation of methylmercury near the water surface.

Whole-water total mercury concentrations ranged from 1.43 to 7.02 nanograms per liter for the wetland site (site 1), from 0.38 to 2.98 nanograms per liter for the Devils Lake sites (sites 3 through 7), and from 0.63 to 3.11 nanograms per liter for the Lake Ashtabula sites (sites 9 and 10) (supplement 5; fig. 8). These concentrations are less than 10 nanograms per liter, which might be considered the upper end of the range of typical aquatic concentrations throughout the United States (Hurley and others, 1995; Krabbenhoft and others, 1999). Whole-water total mercury concentrations for the lakes and wetland sampled for this investigation were similar to concentrations reported for natural lakes in the Red River of the North Basin in Minnesota (Brigham and others, 1999; Brigham and others, 2002) and Wisconsin (Fitzgerald and Watras, 1989) and to previously reported concentrations for Devils Lake and Lake Ashtabula (table 6) and for other lake sites in the Devils Lake and Sheyenne River Basins (table 7). However, detailed comparison of mercury concentrations from this investigation with previously reported concentrations for Devils Lake and Lake Ashtabula is complicated by (1) differences in sampling locations; (2) differences in the seasonal timing of sampling; and (3) the relatively small number of samples collected.

Among the lake and wetland sites, the wetland site (site 1) had the largest whole-water total mercury concentrations for both sampling periods (1.43 and 7.02 nanograms per liter for the winter and summer sampling periods, respectively). Patterns in whole-water total mercury concentrations in near-surface samples relative to near-bottom samples were not consistent either between sites, or for a given site, between sampling periods. For example, for the winter sampling period, near-bottom concentrations were greater than near-surface concentrations for sites 3, 4, and 10, but near-bottom concentrations were slightly less than near-surface concentrations for sites 5 and 7. For the summer sampling period, the near-bottom concentration was greater than the near-surface concentration for site 7, but near-bottom concentrations were less than near-surface concentrations for sites 3, 5, and 10. Generally, both dissolved and particulate total mercury concentrations were larger for the summer sampling period than for the winter sampling period for the various sites. Except for site 9, particulate total mercury concentrations were small (generally near or less than 0.1 nanogram per liter) for all winter samples.

Masses of mercury constituents for the lake and wetland sites are shown in figure 9. For the wetland site (site 1), methylmercury comprised a substantial part of total mercury for both the winter and summer sampling periods (about 25 percent for the winter sampling period and about 50 percent for the summer sampling period; fig. 7) and was almost entirely in dissolved phase. The summer methylmercury concentration was about 10 times greater than the winter methylmercury concentration, and most of the methylmercury comprising the increase was in dissolved phase. This indicates that the wetland site has favorable conditions for methylation of mercury and that production of methylmercury in the sediments is a primary factor governing mercury processes in the wetland. Although most of the mercury was in dissolved phase, a substantial increase also occurred between winter and summer particulate total mercury masses (fig. 9).

For Devils Lake, the mass of mercury in winter was small relative to summer (fig. 9), and the mercury was mostly in dissolved inorganic phase. The whole-water total mercury mass increased substantially (about 4 times) between winter and summer, and relatively large increases also occurred in both dissolved and particulate methylmercury. At the shallow more-upstream sites (sites 3 and 4), the increase in methylmercury between winter and summer was almost entirely in particulate phase. The morphologic and limnologic characteristics at those sites may result in greater interaction and

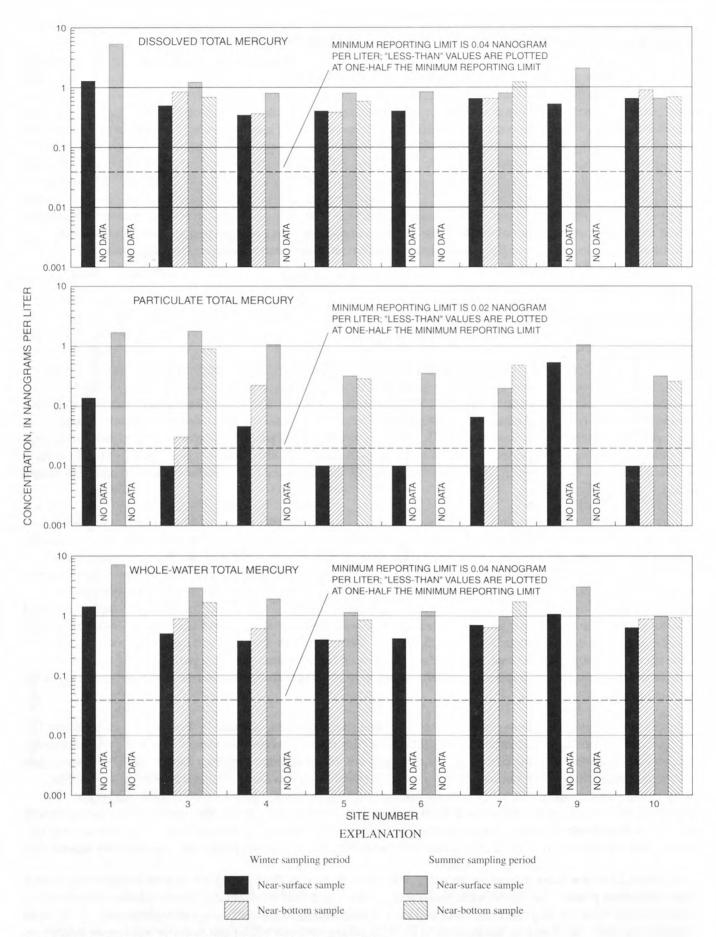


Figure 8. Concentrations of total mercury for lake and wetland sites.

Table 6. Concentrations of mercury constituents for Devils Lake and Lake Ashtabula, 1991-93 [Wayne R. Berkas, U.S. Geological Survey, written commun., 2001; ng/L, nanograms per liter; --, no data]

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Site number (see figure 1 for location)	Site identification number	Site name	Date	Methylmercury, dissolved (ng/L)			Total mercury, dissolved (ng/L)			Total mercury, whole water (ng/L)		
				Near surface	Mid- depth	Near bottom	Near surface	Mid- depth	Near bottom	Near surface	Mid- depth	Near bottom
	480623099013400	Devils Lake Six Mile Bay	09/19/91							2.80		
	480500098561000	Devils Lake Creel Bay	09/18/91							2.60		
			03/22/93			0.06	0.66	0.90	1.45			
5	480147098572200	Devils Lake Main Bay	09/19/91				2.10		.20	3.20		
		•	02/15/92				1.00	1.00	1.00	2.30	1.70	2.00
			03/22/93			.10	.69	.90	.66			
	480407098491900	Devils Lake East Bay West	09/19/91				1.00			1.30		
7	475740098381600	East Devils Lake	09/18/91				1.60					
			02/15/92				.40	1.80	1.00	1.10	2.00	1.00
			03/23/93			.09	.75	1.08	.13			
10	05057500	Lake Ashtabula at Baldhill Dam, North Dakota	03/10/93				.92		.50			

Table 7. Concentrations of mercury constituents for selected lakes in the Devils Lake and Sheyenne River Basins, 1991-93 [Wayne R. Berkas, U.S. Geological Survey, written commun., 2001; ng/L, nanograms per liter; --, no data]

Site identification	Site name	Date	Met	hylmercury, dissol (ng/L)	ved	Total mercury, dissolved (ng/L)			
number			Near surface	Mid-depth	Near bottom	Near surface	Mid-depth	Near bottom	
481335098492000	Sweetwater Lake near Webster	09/19/91						11.40	
475150098210000	East Stump Lake near Perkin	09/18/91				i		6.40	
475350098501300	Wood Lake	03/23/93				0.45		1.56	
474844098363800	Battle Lake	03/23/93				2.51			
480032101314701	Rice Lake near Ryder	03/11/93				1.59			
480137100011600	Round Lake north of Anamoose	03/11/93						.37	
470427098345800	Spiritwood Lake	03/15/93	0.03	0.04		.93	0.50		
473407097371600	Golden Lake	03/15/93				.64			

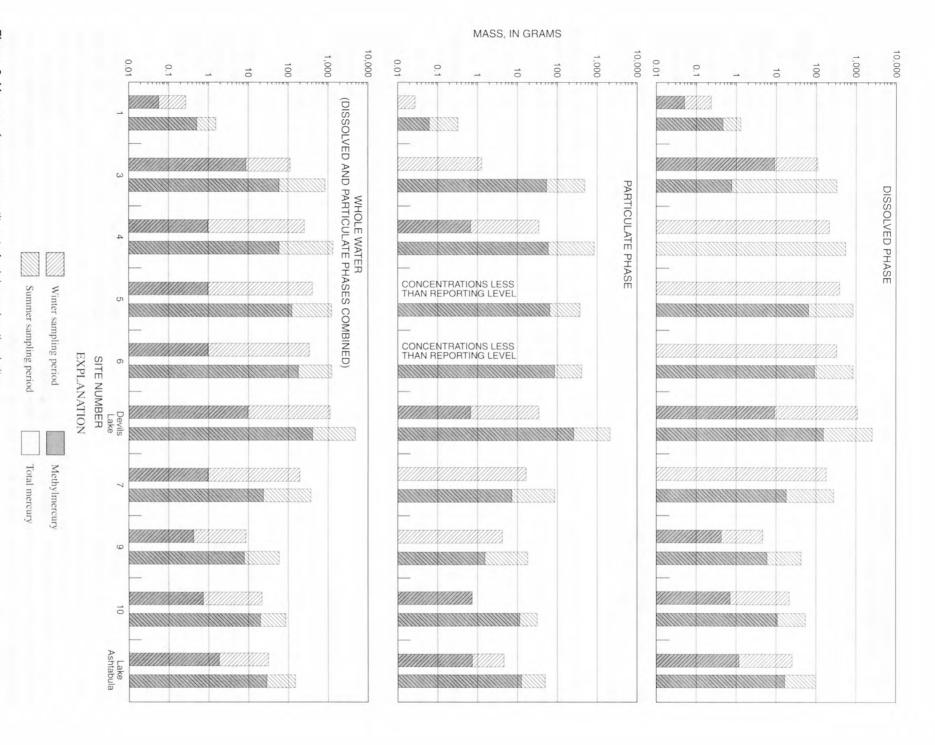


Figure 9. Masses of mercury constituents for lake and wetland sites

mixing between near-bottom areas and the entire water column, causing more particulate material (both organic and inorganic), to which methylmercury adsorbs, to be suspended throughout the water column. At the deep more-downstream sites (sites 5 and 6), the increase in methylmercury between winter and summer was substantial for both dissolved and particulate phases. The characteristics at those sites may result in more stable stratification between the hypolimnion and the upper water column, thus maintaining a larger part of methylmercury in dissolved phase. However, substantial adsorption of methylmercury to particulate material still occurs. Most of the whole-water total mercury mass was in dissolved inorganic phase (about 90 percent in winter and 50 percent in summer), indicating that (1) besides the methylmercury that is being mobilized from the sediments by methylation of mercury, other important sources of mercury exist and/or (2) the methylmercury that is being mobilized from the sediments is transformed to both dissolved and particulate inorganic phases. Mechanisms that can transform methylmercury to inorganic mercury include microbiallymediated demethylation and photochemical degradation (Krabbenhoft, 1996; Krabbenhoft and others, 2000). Generally, conditions suitable for methylation of mercury exist throughout the Devils Lake system. Ratios of whole-water methylmercury to whole-water total mercury in summer near-bottom samples ranged from about 15 to 20 percent at the Devils Lake sites (sites 3 through 7) (fig. 7). However, methylation of mercury in Devils Lake probably occurs at much smaller rates than in the wetland, where the summer ratio was about 50 percent. It appears from this reconnaissance investigation that mercury in Devils Lake exhibits an annual cycle with a summer maximum. Mercury may be removed from the water column following the summer maximum by (1) adsorption to particulate material with subsequent deposition to the sediments; (2) volatilization; and/or (3) uptake and bioaccumulation by aquatic organisms (Krabbenhoft and Rickert, 1995).

For Lake Ashtabula, as for Devils Lake, the mass of mercury in winter was small relative to summer (fig. 9), and the mercury was mostly in dissolved inorganic phase. Dissolved inorganic mercury accounted for about 80 percent of the total mercury mass in winter and about 50 percent in summer. The whole-water total mercury mass increased substantially between the winter and summer sampling periods (about 4 times), and relatively large increases also occurred in both dissolved and particulate methylmercury. Methylmercury accounted for a relatively large proportion of total mercury in Lake Ashtabula (fig. 7), especially at the deep site (site 10) near the dam. For site 9, the shallow more-upstream site, most of the methylmercury was in dissolved phase. For site 10, the deep more-downstream site near the dam, the winter nearbottom sample had substantially larger methylmercury concentrations than the winter near-surface sample. However, the summer near-bottom and near-surface samples had similar concentrations (fig. 7). Also, the ratio of whole-water methylmercury to whole-water total mercury increased substantially between winter and summer near-surface samples. Although field-measured properties and constituents showed fairly strong thermal stratification on the sampling days for both the winter and summer sampling periods for site 10, the hydrologic and limnologic characteristics of Lake Ashtabula (that is, the pattern of dam releases and the movement of water through the reservoir) may result in greater interaction and mixing between near-bottom areas and the entire water column throughout the lake. Thus, methylmercury produced at the sediment-water interface may be exposed to suspended material (to which it can adsorb) throughout the water column. Lake Ashtabula probably has conditions favorable for methylation of mercury throughout most of the lake, and the flowthrough characteristics of the reservoir may result in more even distribution of methylmercury throughout the water column during summer.

Spearman's rank-correlation procedure (Iman and Conover, 1983) was used to investigate relations between mercury constituents and other water-quality properties and constituents for the lake and wetland sites (table 8). Concentrations for all samples collected for the lake and wetland sites were included in the data set that was analyzed. Thus, sites where both near-surface and near-bottom samples were collected had greater weight in the analysis than sites where only near-surface samples were collected. However, differences between near-surface and near-bottom environments at a given site provide useful information for discerning relations between mercury constituents and other water-quality properties and constituents.

Generally, concentrations of individual mercury constituents in lakes and wetlands were correlated significantly with other mercury constituents. This result might indicate that mercury is cycled between organic and inorganic phases and also between dissolved and particulate phases. All mercury constituents were correlated positively with water temperature. This result is consistent with observations of higher concentrations of mercury constituents in summer than in winter and also might provide evidence that methylation plays an important role in contributing mercury to the water column. Microbial breakdown of organic matter by sulfate reduction typically occurs at higher rates when temperatures increase (Rheinheimer, 1974) and might result in higher mercury methylation rates. Most mercury constituents were correlated

 Table 8. Statistically significant results of Spearman's rank-correlation procedure to investigate relations between mercury constituents and other water-quality properties and constituents for lake and wetland sites

Manana	Positive statistically sign	ificant correlations	Negative statistically significant correlations ¹			
Mercury constituent	Property or constituent	Spearman's p-value		Property or constituent	Spearman's rho	p-value
Dissolved	Particulate methylmercury	0.442	0.0304	Specific conductance	-0.432	0.0344
methylmercury	Whole-water methylmercury	0.910	0	pH	-0.531	0.0093
	Dissolved total mercury	0.702	0.0006	Dissolved oxygen	-0.540	0.008
	Particulate total mercury	0.401	0.0499			
	Whole-water total mercury	0.592	0.0037			
	Water temperature	0.448	0.0284			
	Whole-water manganese	0.480	0.0244			
Particulate	Dissolved methylmercury	0.442	0.0304	Specific conductance	-0.429	0.035
methylmercury	Whole-water methylmercury	0.708	0.0005			
	Dissolved total mercury	0.616	0.0026			
	Particulate total mercury	0.862	0			
	Whole-water total mercury	0.822	0.0001			
	Water temperature	0.851	0			
	Suspended sediment	0.538	0.0268			
Whole-water	Dissolved methylmercury	0.910	0	Specific conductance	-0.593	0.003
methylmercury	Particulate methylmercury	0.708	0.0005	Dissolved oxygen	-0.417	0.040
	Dissolved total mercury	0.800	0.0001	Dissolved sulfate	-0.432	0.042
	Particulate total mercury	0.620	0.0024			
	Whole-water total mercury	0.780	0.0001			
	Water temperature	0.678	0.0009			
	Suspended sediment	0.496	0.0411			
Dissolved	Dissolved methylmercury	0.702	0.0006			
total mercury	Particulate methylmercury	0.616	0.0026			
	Whole-water methylmercury	0.800	0.0001			
	Particulate total mercury	0.535	0.0088			
	Whole-water total mercury	0.859	0			
	Water temperature	0.611	0.0028			
	Suspended sediment	0.684	0.0048			
Particulate	Dissolved methylmercury	0.401	0.0499	Specific conductance	-0.408	0.045
total mercury	Particulate methylmercury	0.862	0			
	Whole-water methylmercury	0.620	0.0024			
	Dissolved total mercury	0.535	0.0088			
	Whole-water total mercury	0.866	0			
	Water temperature	0.698	0.0006			
	Suspended sediment	0.620	0.0107			
Whole-water	Dissolved methylmercury	0.592	0.0037	Specific conductance	-0.447	0.028
total mercury	Particulate methylmercury	0.822	0.0001	Specific Conductance	54.1.1	020
	Whole-water methylmercury	0.780	0.0001			
	Dissolved total mercury	0.859	0.0001			
	Particulate total mercury	0.866	0			
	Water temperature	0.739	0.0003			
	Suspended sediment	0.702	0.0039			

¹Statistical significance based on $\alpha = 0.05$; that is, p-value less than 0.05.

positively with suspended sediment, indicating the affinity for mercury to adsorb to particulate material and to cycle between dissolved and particulate phases in the lakes and wetlands. Dissolved methylmercury was correlated negatively with specific conductance, pH, and dissolved oxygen. Sulfate reduction occurs in low dissolved-oxygen environments, and low pH values have been reported to be associated with methylation of mercury (U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service, 1996). The negative association between methylmercury and specific conductance is unclear but may be related to sulfate inhibition of methylation. Sulfate generally is the dominant anion contributing to the ionic strength of the lakes and wetlands sampled for this investigation. Large concentrations of sulfate have been reported to inhibit methylation of mercury because of an accumulation of sulfide that can bind available mercury ions (U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service, 1996). However, negative correlations between mercury constituents and sulfate individually were not as strong as between mercury constituents and specific conductance. Also, the biological and chemical interactions that affect sulfate reduction, availability of mercury for methylation, and the inhibitory effects of sulfide on methylation of mercury are complex and site specific; previously reported patterns in sulfate inhibition of methylation do not appear to directly apply to the lakes and wetlands sampled for this investigation.

Rivers

Whole-water methylmercury concentrations in water samples from river sites were relatively large and ranged from 0.45 to 1.13 nanograms per liter for the Starkweather Coulee site (site 2), from 0.20 to 1.44 nanograms per liter for the Sheyenne River sites (sites 8, 11, and 12), and from 0.15 to 0.47 nanogram per liter for the Red River of the North and Red Lake River sites (sites 13 through 16) (supplement 6; fig. 10). Most sites had methylmercury concentrations that exceeded 0.10 nanogram per liter, which might be considered the upper end of the range of typical aquatic concentrations throughout the United States (Krabbenhoft and others, 1999). However, the concentrations were only slightly larger than concentrations reported for streams in Wisconsin drainage basins that were dominated by wetlands, agriculture, and/or forested areas (Hurley and others, 1995). Generally, methylmercury concentrations for most sites increased between spring and summer for both dissolved and particulate phases, and most of the increase was caused by methylmercury in particulate phase. Starkweather Coulee (site 2), which drains an area dominated by wetlands, had the largest dissolved methylmercury concentrations for both sampling periods. The summer concentration for site 2 was very large, indicating that conditions in the Starkweather Coulee channel or in water bodies that flow into the channel were favorable for methylation of mercury. According to Hurley and others (1995), streams that drain wetland areas tend to have larger methylmercury concentrations than streams that drain either agricultural or forested areas. Methylmercury concentrations also were large for the Sheyenne River near Kindred (site 12). Concentrations increased between sites 11 and 12 for both sampling periods, and most of the increase was caused by methylmercury in particulate phase. Thus, methylation conditions may be favorable in the Sheyenne River channel between sites 11 and 12 or in water bodies that flow into that reach. Also, methylmercury concentrations between sites 11 and 12 may be affected by channel hydraulics and morphology and the degree to which sediments are resuspended and transported at the two sites. Lake Ashtabula is located between sites 8 and 11 and methylmercury concentrations generally are similar between the two sites. However, for the sampling period, methylmercury concentrations increased between the two sites. Also, the summer ratio of whole-water methylmercury to whole-water total mercury for site 11 (13.5 percent) was larger than for either site 8 (3.5 percent) or site 12 (11.0 percent) (fig. 10). These patterns may indicate favorable conditions for methylation of mercury in Lake Ashtabula. Ratios of whole-water methylmercury to whole-water total mercury were less than 8 percent for the Red River of the North or Red Lake River sites (fig. 10).

Whole-water total mercury concentrations ranged from 3.22 to 6.33 nanograms per liter for the Starkweather Coulee site (site 2), from 2.00 to 17.84 nanograms per liter for the Sheyenne River sites (sites 8, 11, and 12), and from 5.73 to 26.90 nanograms per liter for the Red River of the North and Red Lake River sites (sites 13 through 16) (supplement 6; fig. 11). Generally, the concentrations were small to moderately large. Only a few samples had concentrations that exceeded 10 nanograms per liter, which might be considered the upper end of the range of typical aquatic concentrations at locations where the dominant sources of mercury are naturally occurring or result from atmospheric deposition (Krabbenhoft, 1996). Whole-water total mercury concentrations for rivers sampled for this investigation also were generally similar to concentrations reported for uncontaminated streams in Wisconsin (Hurley and others, 1995); generally similar to concentrations reported for the Minnesota River, which is in an agriculture-dominated basin in South Dakota, Minnesota, and Iowa (Balogh and others, 1997); and generally larger than concentrations reported for the St. Croix and upper Mississippi Rivers in Minnesota, which are in basins that are dominated by uncultivated forest and wetland areas

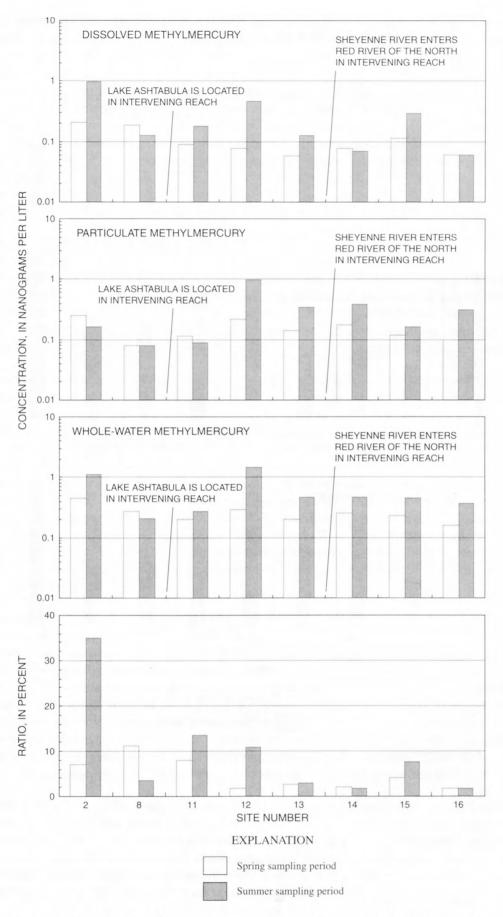


Figure 10. Concentrations of methylmercury and ratios of whole-water methylmercury to whole-water total mercury for river sites.

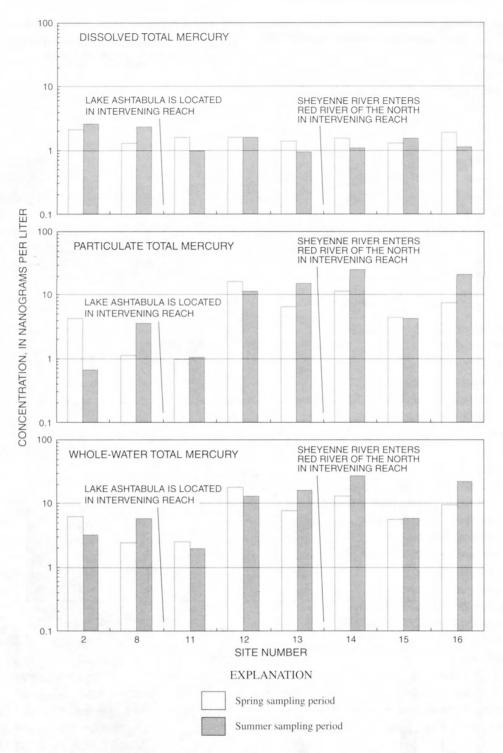


Figure 11. Concentrations of total mercury for river sites.

(Balogh and others, 1998). For Starkweather Coulee (site 2) and the two most-upstream sites on the Sheyenne River (sites 8 and 11), dissolved total mercury concentrations generally were similar to particulate total mercury concentrations. For sites 12 through 16, particulate total mercury accounted for most of the whole-water total mercury. However, particulate total mercury concentrations decreased between sites 8 and 11, possibly indicating that Lake Ashtabula acts as a sink for that constituent. The large increase in particulate total mercury concentrations between sites 11 and 12 was similar in magnitude to the increase in suspended-sediment concentrations for those sites (fig. 5) and probably indicates that mercury at site 12 primarily is inorganic and adsorbed to suspended sediment. Total mercury concentrations for the Sheyenne River and Red Lake River sites generally were similar for the spring and summer sampling periods, but concentrations for the Red River of the North sites generally increased during the summer sampling period. The differences between spring and summer concentrations may be a result of site-specific differences in composition of suspended sediment and partitioning of mercury between dissolved and various particulate phases (Hurley and others, 1995). Whole-water total mercury concentrations at all sites were at levels that would not be considered extreme.

Loads of mercury constituents for the river sites are shown in figure 12. Consideration of the loads for the river sites is particularly relevant to the purpose of this report. If an outlet from Devils Lake to the Sheyenne River is constructed, discharge of the Sheyenne River downstream from the proposed diversion will increase. Although the mixing of water from Devils Lake with the Sheyenne River may or may not result in substantial differences in concentrations of mercury constituents in the Sheyenne River, the mixing will result in an increase in the load of mercury transported in the river. An understanding of how loads of mercury constituents currently are transported in the Sheyenne River and the Red River of the North will aid in assessing the effects of increased mercury loads downstream from the proposed outlet.

Direct comparison of loads between sampling sites within a given sampling period is complicated by relative differences in discharge conditions that may have existed between the sites at the time of sampling. In addition to discharge being a variable in the calculation of loads, discharge also can strongly affect mercury concentrations. Mercury can readily adsorb to suspended particulate material and concentrations of suspended particulate material in streams is strongly dependent on flow conditions (Grigal, 2002). Discharges for the Sheyenne River, Red River of the North, and Red Lake River sites are shown in figure 13, and nonexceedance frequencies for the discharges at the time of sampling are given in table 9. The nonexceedance frequencies provide information on flow conditions at the time of sampling relative to typical flow conditions for that time of year. Nonexceedance frequencies were determined by statistically comparing discharges on the specific day of sampling with daily discharges for the same day for the entire period of record for the site. For example, a nonexceedance frequency of 90 percent for the Sheyenne River near Warwick (table 9) for April 30, 2001, indicates that a discharge of 460 cubic feet per second exceeds 90 percent of all daily discharges recorded at the site on April 30 for the entire period of record. Thus, a nonexceedance frequency of 90 percent would indicate much-above-normal flow conditions for the given day.

The hydrographs and the times of sampling for the river sites (fig. 13) indicate that for the spring sampling period, all samples were collected on receding limbs of large runoff events. Nonexceedance frequencies for the Sheyenne River, Red River of the North, and Red Lake River sites ranged from 81 to 97 percent and indicate that spring flow conditions were much-above normal. Flows steadily declined after the peak snowmelt runoff in early April except for a few relatively minor runoff events. For the summer sampling period, flow conditions at all sites also were fairly similar. Generally, the summer samples were collected near the peak or on receding limbs of relatively small runoff events. Nonexceedance frequencies for the summer sampling period (table 9) ranged from 79 to 96 percent and again indicate that flow conditions at all sites were much-above normal. Generally, flow conditions for both sampling periods were reasonably similar among the different sites relative to timing with respect to runoff events and also relative to typical flow conditions for the given times of year. Thus, coarse comparisons of loads of mercury constituents between the different sites are justified.

For Starkweather Coulee (site 2), the loads of total mercury decreased substantially between the spring and summer sampling periods (fig.12), primarily because of a decrease in discharge of about 75 percent (supplement 2). However, even with the substantial decrease in discharge, the load of dissolved methylmercury increased between spring and summer, and the summer ratio of whole-water methylmercury to whole-water total mercury was 35 percent (fig. 10). Thus, the observation that the Starkweather Coulee channel and/or water bodies that flow into the channel have favorable conditions for methylation of mercury, especially during summer, is further supported.

For the Sheyenne River, loads of whole-water total mercury generally were small at sites 8 and 11 for both sampling periods and increased substantially at site 12, especially for the spring sampling period (fig. 12). For the spring sampling

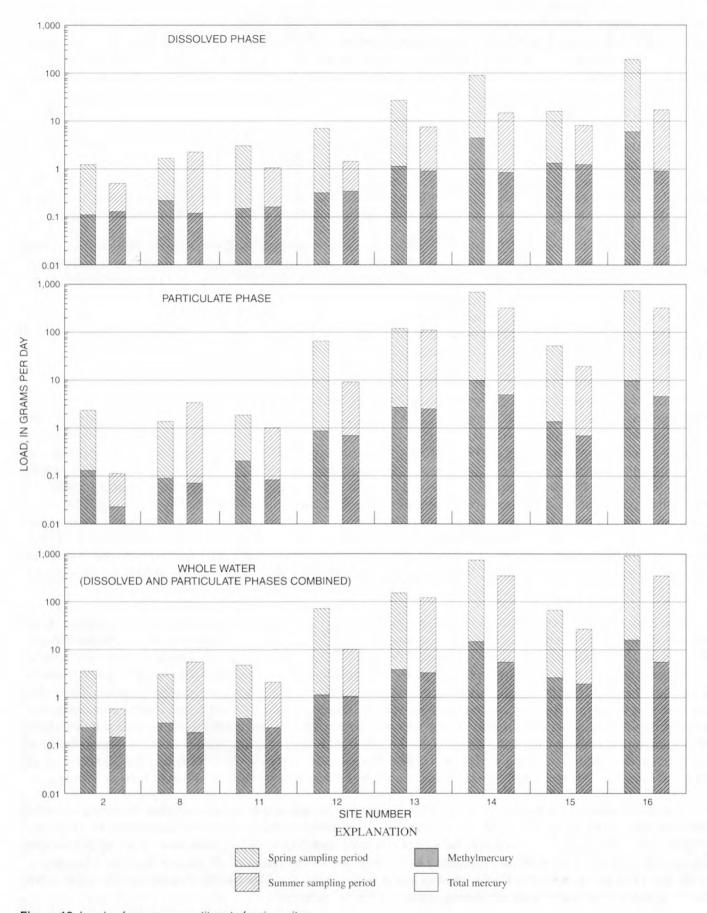


Figure 12. Loads of mercury constituents for river sites.

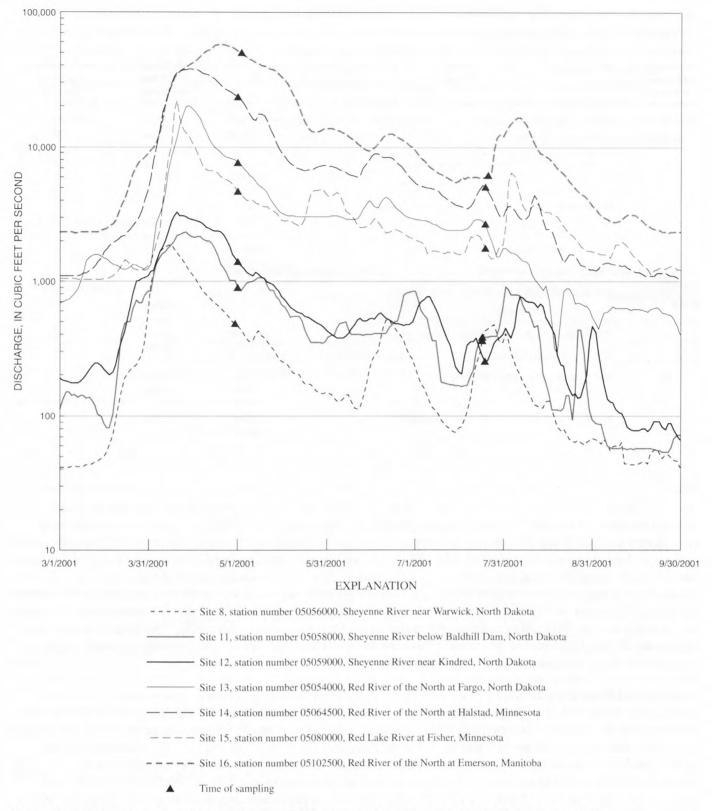


Figure 13. Discharge and times of sampling for the Sheyenne River, Red River of the North, and Red Lake River sites.

Table 9. Nonexceedance frequencies for discharges at time of sampling for river sites [--, not determined]

Site number (see figure 1 for location)	Site name	Date	Discharge (cubic feet per second)	Nonexceedance frequency (percent)
2	Starkweather Coulee near Webster, North Dakota	04/30/01 07/24/01	220 56	89 70
8	Sheyenne River near Warwick, North Dakota	04/30/01 07/24/01	460 380	90 96
11	Sheyenne River below Baldhill Dam, North Dakota	05/01/01 07/24/01	720 370	81 84
12	Sheyenne River near Kindred, North Dakota	05/01/01 07/25/01	1,650 290	86 79
13	Red River of the North at Fargo, North Dakota	05/01/01 07/25/01	7,700 2,880	97 96
14	Red River of the North at Halstad, Minnesota	05/01/01 07/25/01	23,500 5,050	95 93
15	Red Lake River at Fisher, Minnesota	05/01/01 07/25/01	4,660 1,760	
16	Red River of the North at Emerson, Manitoba	05/02/01 07/26/01	40,000 6,100	

period, particulate total mercury loads were similar between sites 8 and 11 although discharge increased by about 60 percent between the two sites. For the summer sampling period, particulate and whole-water total mercury loads decreased between sites 8 and 11 although discharges were similar between the two sites. These patterns possibly indicate the effects of Lake Ashtabula as a mercury sink. The larger whole-water total mercury loads at site 12 occurred primarily in the particulate inorganic phase and probably are a function of increased suspended-sediment transport at site 12. Ratios of whole-water methylmercury to whole-water total mercury generally were near or less than 10 percent for the Sheyenne River sites. The largest ratio for any Sheyenne River site (13.5 percent) was recorded at site 11 for the summer sampling period and may indicate favorable conditions for methylation of mercury in Lake Ashtabula. The loads of whole-water total mercury for site 12 decreased substantially between the spring and summer sampling periods, primarily because of a decrease in discharge of about 82 percent (supplement 2).

For the Red River of the North, loads of total mercury increased substantially between sites 13 and 14 for both sampling periods (fig. 12). The Sheyenne River enters the Red River of the North in the intervening reach, but the increase in load between the two sites was much larger than can be accounted for by inputs from the Sheyenne River. For example, the loads of whole-water total mercury transported in the Sheyenne River near Kindred (site 12) were about 70 and 10 grams per day for the spring and summer sampling periods, respectively, but the increases in loads between sites 13 and 14 were about 600 and 200 grams per day for the spring and summer sampling periods, respectively. The substantial increase in load between sites 13 and 14 indicates that important sources of mercury, in addition to the Sheyenne River, exist in the intervening reach. These sources of mercury may include contributions from other tributaries, flux of mercury from stream sediments, atmospheric deposition, and various sources associated with the city of Fargo. Loads of mercury for sites 14 and 16 were similar although a 70-percent increase in discharge occurred between the two sites during the spring sampling period (supplement 2). This may indicate that tributary inflows between the two sites had negligible loads of mercury and/or that various processes that remove mercury from the water column were occurring between the two sites. Possible mechanisms for removal of mercury from the water column include volatilization, deposition in sediments, and uptake by biota (Krabbenhoft and Rickert, 1995).

Results of Spearman's rank-correlation procedure (Iman and Conover, 1983) for the river sites (table 10) indicated dissolved methylmercury was correlated positively with organic-carbon constituents and negatively with discharge. This pattern may indicate that smaller tributaries in wetland-dominated basins may serve as primary areas for the production of methylmercury and from which methylmercury is contributed to the river systems. Total mercury constituents generally were correlated positively with discharge and suspended sediment. These relations, along with the fact that nearly all mercury in the water at the river sites is in inorganic particulate phase (figs. 10 and 11), support previous observations that processes that result in mobilization, suspension, and transport of sediment largely govern concentrations of total mercury for the river sites. The strong correlation between whole-water total mercury concentrations and suspended-sediment concentrations is similar to relations reported for sites on the Minnesota River (Balogh and others, 1997).

Table 10. Statistically significant results of Spearman's rank-correlation procedure to investigate relations between mercury constituents and other water-quality properties and constituents for river sites

	Positive statistically signif	icant correlation	ns ¹	Negative statistically sign	ificant correlation	ons ¹
Mercury constituent	Property or constituent	Spearman's rho	p-value	Property or constituent	Spearman's rho	p-value
Dissolved methylmercury	Whole-water methylmercury	0.6024	0.0200	Discharge	-0.8542	0.0009
	Dissolved organic carbon	0.7364	0.0044	Particulate total mercury	-0.5287	0.0400
	Whole-water organic carbon	0.7761	0.0027			
Particulate methylmercury	Dissolved calcium	0.5725	0.0270			
	Whole-water methylmercury	0.7294	0.0048			
	Particulate total mercury	0.6971	0.0071			
	Whole-water total mercury	0.7824	0.0025			
	Suspended sediment	0.6434	0.0164			
Whole-water methylmercury	Water temperature	0.6824	0.0084	Dissolved oxygen	-0.5092	0.0480
	Dissolved calcium	0.6416	0.0132			
	Dissolved methylmercury	0.6024	0.0200			
	Particulate methylmercury	0.7294	0.0048			
Dissolved total mercury	Whole-water manganese	0.7563	0.0489			
Particulate total mercury	Discharge	0.5853	0.0238	Dissolved potassium	-0.5313	0.0391
	Whole-water total mercury	0.9529	0.0002	Dissolved sulfate	-0.5618	0.0292
	Suspended sediment	0.8668	0.0012	Dissolved organic carbon	-0.7029	0.0064
				Whole-water organic carbon	-0.7324	0.0045
Whole-water total mercury	Suspended sediment	0.8758	0.0011	Dissolved organic carbon	-0.6765	0.0064
				Whole-water organic carbon	-0.6971	0.0068

¹Statistical significance based on $\alpha = 0.05$; that is, p-value less than 0.05.

Possible Effects from Devils Lake Outlet

The proposed plans for an outlet from Devils Lake include pumping water from the southern part of Devils Lake West Bay, an area represented by site 4 in this investigation, into the Sheyenne River channel in the reach between sites 8 and 9. Although the number of samples collected during this investigation is small, results indicated concentrations of both methylmercury and total mercury constituents for site 4 were less than concentrations for site 8 for both sampling periods. Thus, an outlet probably would not have adverse effects on mercury concentrations in the Sheyenne River upstream from Lake Ashtabula. However, because discharges in the Sheyenne River would increase during some periods, the loads of mercury entering Lake Ashtabula also would increase. To completely evaluate the effects of the increased loads into Lake Ashtabula, further data collection is needed. However, some general observations can be made. Lake Ashtabula probably

serves as a sink for suspended sediment (fig. 5) and whole-water total mercury (fig. 11) and most of the whole-water total mercury that occurs in the downstream part of the Sheyenne River originates downstream from Lake Ashtabula. Thus, a Devils Lake outlet probably would not have substantial effects on mercury concentrations or loads in the downstream part of the Sheyenne River or in the Red River of the North. More substantial effects could occur for Lake Ashtabula. Lake Ashtabula is a hypereutrophic lake and conditions for methylation of mercury can be favorable, as evidenced by large methylmercury concentrations and large ratios of whole-water methylmercury to whole-water total mercury (fig. 7). The fact that loads of mercury in the Sheyenne River downstream from Lake Ashtabula are slightly less than loads upstream from Lake Ashtabula may indicate that processes that prevent transport of methylmercury downstream are occurring in Lake Ashtabula. These processes could include sedimentation, demethylation and subsequent volatilization, and/or uptake and bioaccumulation by aquatic organisms (Krabbenhoft and Rickert, 1995). A detailed study of the mass balance of mercury constituents in Lake Ashtabula and the Sheyenne River would be needed to fully address the fate of mercury in Lake Ashtabula and the possible effects of a Devils Lake outlet on mercury in Lake Ashtabula.

SUMMARY AND CONCLUSIONS

Devils Lake rose dramatically during the 1990's, and flood damages in the Devils Lake Basin have exceeded \$400 million. Because of the potential for continued lake-level rises and the potential for additional damages, the U.S. Army Corps of Engineers has been conducting engineering and environmental studies to evaluate the feasibility of constructing and operating an outlet from Devils Lake. The occurrence of mercury in the Red River of the North Basin and the potential for increased loading of mercury into the Sheyenne River as a result of a constructed outlet from Devils Lake needed to be considered and evaluated as part of the studies.

Water samples were collected at 16 lake, wetland, and river sites in the Devils Lake, Sheyenne River, Red River of the North, and Red Lake River Basins and analyzed for selected field-measured properties and constituents and laboratory-measured major-ion, trace-element, suspended-sediment, mercury, and organic-carbon constituents. Lake and wetland sites were sampled in winter during ice cover and in late summer during peak heating conditions. River sites were sampled during spring-runoff conditions and in late summer during low-flow/peak heating conditions.

Generally, the lake and wetland sites tended to be moderately alkaline and of relatively high ionic strength. Deep lake sites generally showed relatively strong thermal stratification with substantial near-bottom dissolved oxygen depletion during both winter and summer sampling periods, and shallow lake sites did not show strong thermal stratification in either sampling period. River sites tended to be moderately alkaline and of moderate ionic strength. Dissolved-oxygen concentrations generally were near saturation during spring-runoff conditions and no more than moderately depleted during the summer sampling period. For all sampling sites, sulfate concentrations were much larger than the minimum concentration required for sulfate reduction and also were much larger than concentrations reported to inhibit methylation of mercury. However, biological and chemical interactions that affect sulfate reduction and the inhibitory effects of sulfide on methylation of mercury are complex and site specific.

Whole-water methylmercury concentrations for the lake and wetland sites ranged from 0.39 to 3.53 nanograms per liter for the wetland site, from less than 0.04 to 0.34 nanogram per liter for the Devils Lake sites, and from less than 0.04 to 0.46 nanogram per liter for the Lake Ashtabula sites. For the winter sampling period, most of the methylmercury in water samples from the lake and wetland sites was in dissolved phase, and concentrations generally were less than the reporting level of 0.04 nanogram per liter. Summer methylmercury concentrations generally were greater than winter methylmercury concentrations, and the whole-water methylmercury concentration for the wetland site was large. However, summer particulate methylmercury concentrations were relatively larger than winter concentrations, probably because of larger amounts of suspended particulate organic and inorganic materials that adsorb mercury during summer. Generally, near-bottom samples had larger dissolved methylmercury concentrations than near-surface samples for both sampling periods, possibly indicating production of methylmercury by sulfate reduction at the sediment-water interface and/or photodegradation of methylmercury near the water surface.

For the lake and wetland sites, whole-water total mercury concentrations ranged from 1.43 to 7.02 nanograms per liter for the wetland site, from 0.38 to 2.98 nanograms per liter for the Devils Lake sites, and from 0.63 to 3.11 nanograms per liter for the Lake Ashtabula sites. The wetland site had the largest whole-water total mercury concentrations for both sampling periods (1.43 and 7.02 nanograms per liter for the winter and summer sampling periods, respectively). Both

dissolved and particulate total mercury concentrations were larger for the summer sampling period than for the winter sampling period for the various sites. Relative differences in total mercury concentrations between near-surface samples and near-bottom samples varied among the sites.

For the wetland site, methylmercury comprised a substantial part of total mercury for both the winter and summer sampling periods (about 25 to 50 percent) and was almost entirely in dissolved phase. The summer methylmercury concentration was about 10 times greater than the winter methylmercury concentration, and most of the methylmercury comprising the increase was in dissolved phase. This indicates that the wetland site has favorable conditions for methylation of mercury and that production of methylmercury in the sediments is a primary factor governing mercury processes in the wetland.

For Devils Lake, the mass of mercury in winter was small relative to summer, and the mercury was mostly in dissolved inorganic phase. The whole-water total mercury mass increased substantially between winter and summer, and relatively large increases also occurred in both dissolved and particulate methylmercury. At the shallow more-upstream sites, the increase in methylmercury between winter and summer was almost entirely in particulate phase. The morphologic and limnologic characteristics at those sites may result in greater interaction and mixing between near-bottom areas and the entire water column, causing more particulate material, to which methylmercury adsorbs, to be suspended throughout the water column. At the deep more-downstream sites, the increase in methylmercury between winter and summer was substantial for both dissolved and particulate phases. The characteristics at those sites may result in more stable stratification between the hypolimnion and the upper water column, thus maintaining a larger part of methylmercury in dissolved phase. However, substantial adsorption of methylmercury to particulate material still occurs. Most of the wholewater total mercury mass was in dissolved inorganic phase, indicating that besides the methylmercury that is being mobilized from the sediments by methylation of mercury, other important sources of mercury exist and/or methylmercury that is being mobilized from the sediments is transformed to both dissolved and particulate inorganic phases. Generally, conditions suitable for methylation of mercury exist throughout the Devils Lake system. Ratios of whole-water methylmercury to whole-water total mercury in summer near-bottom samples ranged from about 15 to 20 percent at the Devils Lake sites. It appears from this reconnaissance investigation that mercury in Devils Lake exhibits an annual cycle with a summer maximum.

For Lake Ashtabula, as for Devils Lake, the mass of mercury in winter was small relative to summer, and the mercury was mostly in dissolved inorganic phase. Dissolved inorganic mercury accounted for about 80 percent of the total mercury mass in winter and about 50 percent in summer. The whole-water total mercury mass increased substantially between the winter and summer sampling periods, and relatively large increases also occurred in both dissolved and particulate methylmercury. Methylmercury accounted for a relatively large proportion of total mercury in Lake Ashtabula, especially at the deep site near the dam. For the shallow more-upstream site, most of the methylmercury was in dissolved phase. For the deep more-downstream site near the dam, the winter near-bottom sample had substantially larger methylmercury concentrations than the winter near-surface sample. However, the summer near-bottom and near-surface samples had similar concentrations. Also, the ratio of whole-water methylmercury to whole-water total mercury increased substantially between winter and summer near-surface samples. Although field-measured properties and constituents showed fairly strong thermal stratification at the deep more-downstream site, the hydrologic and limnologic characteristics of Lake Ashtabula (that is, the pattern of dam releases and the movement of water through the reservoir) may result in greater interaction and mixing between near-bottom areas and the entire water column throughout the lake. Thus, methylmercury produced at the sediment-water interface may be exposed to suspended material (to which it can adsorb) throughout the water column. Lake Ashtabula probably has conditions favorable for methylation of mercury throughout most of the lake, and the flowthrough characteristics of the reservoir may result in more even distribution of methylmercury throughout the water column during summer.

For the river sites, whole-water methylmercury concentrations were relatively large and ranged from 0.45 to 1.13 nanograms per liter for the Starkweather Coulee site, from 0.20 to 1.44 nanograms per liter for the Sheyenne River sites, and from 0.15 to 0.47 nanogram per liter for the Red River of the North and Red Lake River sites. Generally, methylmercury concentrations for most sites increased between spring and summer for both dissolved and particulate phases, and most of the increase was caused by methylmercury in particulate phase. Starkweather Coulee, which drains an area dominated by wetlands, had the largest dissolved methylmercury concentrations for both sampling periods, indicating that conditions in the Starkweather Coulee channel or in the water bodies that flow into the channel were favorable for methylation of mercury. Methylmercury concentrations also were large for the Sheyenne River near Kindred.

Methylmercury concentrations in the Sheyenne River increased between the Sheyenne River below Baldhill Dam site and the Sheyenne River near Kindred site for both sampling periods, and most of the increase was caused by methylmercury in particulate phase. Thus, methylation conditions may be favorable in the Sheyenne River channel between those sites or in water bodies that flow into that reach. Also, methylmercury concentrations between those sites may be affected by channel hydraulics and morphology and the degree to which sediments are resuspended and transported at the two sites. Lake Ashtabula is located between the Sheyenne River near Warwick site and the Sheyenne River below Baldhill Dam site. Although methylmercury concentrations generally are similar between the two sites, patterns in the methylmercury concentrations and in the ratios of whole-water methylmercury to whole-water total mercury may indicate favorable conditions for methylation of mercury in Lake Ashtabula. Ratios of whole-water methylmercury to whole-water total mercury were less than 8 percent for the Red River of the North and Red Lake River sites.

Whole-water total mercury concentrations ranged from 3.22 to 6.33 nanograms per liter for the Starkweather Coulee site, from 2.00 to 17.84 nanograms per liter for the Sheyenne River sites, and from 5.73 to 26.90 nanograms per liter for the Red River of the North and Red Lake River sites. For Starkweather Coulee and the two most-upstream sites on the Sheyenne River, dissolved total mercury concentrations generally were similar to particulate total mercury concentrations. For sites on the downstream part of the Sheyenne River and on the Red River of the North and the Red Lake River, particulate total mercury accounted for most of the whole-water total mercury. However, particulate total mercury concentrations decreased between the Sheyenne River near Warwick site and the Sheyenne River below Baldhill Dam site, possibly indicating that Lake Ashtabula acts as a sink for that constituent. The large increase between the Sheyenne River below Baldhill Dam site and the Sheyenne River near Kindred site was similar in magnitude to the increase in suspended-sediment concentrations for those sites and probably indicates that mercury in the Sheyenne River near Kindred is inorganic and adsorbed to suspended sediment. Total mercury concentrations for the Sheyenne River and Red Lake River sites generally were similar for the spring and summer sampling periods, but concentrations for the Red River of the North sites generally increased during the summer sampling period. The differences between spring and summer concentrations may be a result of site-specific differences in composition of suspended sediment and partitioning of mercury between dissolved and various particulate phases.

For Starkweather Coulee, the loads of total mercury decreased substantially between the spring and summer sampling periods, primarily because of a decrease in discharge of about 75 percent. However, the load of dissolved methylmercury increased between spring and summer, and the summer ratio of whole-water methylmercury to whole-water total mercury was 35 percent. Methylation conditions probably are favorable in the Starkweather Coulee channel or in water bodies that flow into the channel.

For the Sheyenne River, loads of whole-water total mercury generally were small at the Sheyenne River near Warwick and the Sheyenne River below Baldhill Dam sites for both sampling periods and increased substantially at the Sheyenne River near Kindred site, especially for the spring sampling period. Patterns in particulate and whole-water total mercury loads for the Sheyenne River near Warwick and the Sheyenne River below Baldhill Dam sites possibly indicate the effects of Lake Ashtabula as a mercury sink. The larger whole-water total mercury loads at the Sheyenne River near Kindred site occurred primarily in particulate phase and probably are a function of increased suspended-sediment transport at the site. Although the ratios of whole-water methylmercury to whole-water total mercury generally were near or less than 10 percent for the Sheyenne River sites, the largest ratio (13.5 percent) was recorded at the Sheyenne River below Baldhill Dam site for the summer sampling period and may indicate favorable conditions for methylation of mercury in Lake Ashtabula. The loads of whole-water total mercury for the Sheyenne River near Kindred site decreased substantially between the spring and summer sampling periods, primarily because of a decrease in discharge of about 82 percent.

For the Red River of the North, loads of total mercury increased substantially between the Red River of the North at Fargo site and the Red River of the North at Halstad site for both sampling periods. The Sheyenne River enters the Red River of the North in the intervening reach, but the increase in load between the two sites was much larger than can be accounted for by inputs from the Sheyenne River. Other sources of mercury, including contributions from other tributaries, flux of mercury from stream sediments, atmospheric deposition, and various sources associated with the city of Fargo, may be contributing to the increases in mercury loads between Fargo and Halstad. Loads of mercury for the Red River of the North at Halstad and the Red River of the North at Emerson sites were similar although a 70-percent increase in discharge occurred between the two sites during the spring sampling period. This may indicate that tributary inflows between the two sites had negligible loads of mercury or that various processes that remove mercury from the water column were occurring between the two sites.

The proposed plans for an outlet from Devils Lake include pumping water into the Sheyenne River channel. Although the number of samples collected during this investigation is small, results indicated an outlet probably would not have adverse effects on mercury concentrations in the Sheyenne River upstream from Lake Ashtabula. However, because discharges in the Sheyenne River would increase during some periods, the loads of mercury entering Lake Ashtabula also would increase. Lake Ashtabula probably serves as a sink for suspended sediment and whole-water total mercury, and most of the whole-water total mercury that occurs in the downstream part of the Sheyenne River originates downstream from Lake Ashtabula. Thus, a Devils Lake outlet probably would not have substantial effects on mercury concentrations or loads in the downstream part of the Sheyenne River or in the Red River of the North. More substantial effects could occur for Lake Ashtabula. Lake Ashtabula is a hypereutrophic lake and conditions for methylation of mercury can be favorable, as evidenced by large methylmercury concentrations and large ratios of whole-water methylmercury to whole-water total mercury. The fact that loads of mercury in the Sheyenne River downstream from Lake Ashtabula are slightly less than loads upstream from Lake Ashtabula may indicate that processes that prevent transport of methylmercury downstream are occurring in Lake Ashtabula. A detailed study of the mass balance of mercury constituents in Lake Ashtabula and the Sheyenne River would be needed to fully address the fate of mercury in Lake Ashtabula and the possible effects of a Devils Lake outlet on mercury in Lake Ashtabula.

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Supplement 1. Results for field-measured properties and constituents for lake and wetland sites [mm, millimeters; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; --, no data; e, estimated]

Site number (see figure 1 for location)	Site name	Date	Time	Depth at sampling location (feet)	Measure- ment depth (feet)	Barometric pressure (mm of Hg)	Specific conduc- tance, field (µS/cm at 25°C)	pH, field (standard units)	Temper- ature, air (°C)	Temper- ature, water (°C)	Oxygen, dissolved (mg/L)	Oxygen, dissolved (percent saturation)
1	Wetland site in upper Devils Lake Basin	04/30/01 07/31/01	1030 0720			720 714	1,290 1,900	7.7 6.8	17.0 23.0	13.3 21.7	6.2 1.2	63 15
3	Devils Lake West Bay near Pelican Lake	03/15/01	1130 1131 1132 1133 1134 1135	17.1 	2.6 5.9 9.8 13.1 16.4 17.1	728	2,000 1,960 1,960 1,990 2,020 2,020	7.8 7.7 7.7 7.7 7.7 7.6	3.0	.2 1.9 2.6 3.3 3.4 3.5	5.4 5.0 4.0 1.3 1.1	39
		08/01/01	1200 1201 1202 1203	9.2	0 3.3 6.6 9.2	724 	1,200 1,210 1,210 1,200	8.7 8.7 8.7 8.7	23.0	22.9 22.8 22.8 22.7	9.0 8.9 8.8 8.6	111
4	Devils Lake West Bay southwest	03/15/01	1410 1411 1412 1413	12.8	3.3 6.6 9.8 12.8	730	2,340 2,320 2,330 2,320	8.2 8.2 8.2 8.2	7.0 	1 .1 .1	13.0 13.2 13.6 10.9	93
		08/01/01	1420 1421 1422 1423 1424	 	0 3.3 6.6 9.8 13.1		1,850 1,850 1,910 1,950 1,850	8.5 8.5 8.6 8.6 8.6	26.0	23.7 23.7 23.7 23.7 23.7	9.0 8.7 8.6 8.2 8.1	110
5	Devils Lake Main Bay	03/14/01	1000 1001 1002 1003 1004 1005 1006 1007	45.6	2.6 5.9 9.8 13.1 16.4 19.7 23.0 26.2	720	2,280 2,270 2,270 2,270 2,270 2,270 2,260 2,260	8.3 8.3 8.3 8.3 8.3 8.3 8.3	-2.5 	1 1 1 1 1 1 0	12.6 12.6 12.5 12.5 12.5 12.4 12.4 12.3	92
			1007 1008 1009 1010 1011 1012 1013	= 1	29.5 32.8 36.1 39.4 42.7 45.6		2,250 2,240 2,250 2,290 2,420 2,500	8.3 8.3 8.3 8.3 8.2 8.2		.9 1.3 1.7 2.3 2.8 4.1	11.4 9.6 7.4 4.7 3.2	

Supplement 1. Results for field-measured properties and constituents for lake and wetland sites—Continued [mm, millimeters; µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; --, no data; e, estimated]

Site number (see figure 1 for location)	Site name	Date	Time	Depth at sampling location (feet)	Measure- ment depth (feet)	Barometric pressure (mm of Hg)	Specific conduc- tance, field (µS/cm at 25°C)	pH, field (standard units)	Temper- ature, air (°C)	Temper- ature, water (°C)	Oxygen, dissolved (mg/L)	Oxygen, dissolved (percent saturation)
5	Devils Lake Main BayContinued	08/01/01	0815	48.9	0	725	2,040	8.2	19.0	22.0	8.1	98
	A STATE OF THE STA		0816		3.3		2,040	8.3		22.0	7.8	
			0817		6.6		2,040	8.4		22.0	7.7	
			0818		13.1		2,050	8.4		22.0	7.7	44
			0819		19.7		2,050	8.4		22.0	7.7	
			0820		26.2		2,050	8.4		22.0	7.7	
			0821		32.8		2,050	8.4		22.0	7.6	
			0827		39.4		2,050	8.4		21.9	7.3	
			0828		45.9		2,100	8.1		18.2	.5	
			0829		48.9		2,100	8.0		18.0	.4	
6	Devils Lake East Bay	03/14/01	1310	36.4	3.3	722	3,660	8.4	1.5	1	10.7	4.5
O	Deviis Lake Bast Day	03/14/01	1311	50.4	6.6		3,650	8.4		1	10.6	
			1312		9.8		3,660	8.4		1	10.7	
			1313		13.1		3,660	8.4		1	11.0	
			1314		16.4		3,660	8.4		1	11.1	
			1315		19.7		3,680	8.4		1	11.2	-
			1316		23.0		3,670	8.5		1	11.2	
			1317		26.2		3,650	8.5	-	.1	11.1	
			1318		29.5		3,640	8.5		.5	10.0	-
			1319		32.8		3,740	8.4		1.6	6.1	
			1320		36.4		4,020	8.4		2.5	.7	
		08/02/01	0730	38.7	0	731	3,230	8.5	18.0	22.1	7.3	
		00/02/01	0731	50.7	3.3		3,230	8.5	10.0	22.1	7.2	
			0732		6.6		3,230	8.5		22.1	7.1	
			0733		13.1		3,250	8.5		22.1	7.0	
			0734		19.7		3,250	8.5		22.1	6.9	
			0735		26.2	-	3,250	8.5		22.1	6.8	
			0736		32.8		3,230	8.5		22.0	5.0	
			0737		38.7		3,230	8.4		21.6	1.7	
7	East Devils Lake	03/14/01	1525	49.2	3.0	724	6,930	8.4	4.0	2	9.3	68
,	East Devils Lake	03/14/01	1526		6.2	724	6,860	8.4		2	9.0	
			1527		9.2		6,840	8.4		3	8.9	
			1528		13.1		6,830	8.5		3	8.8	
			1529		16.4		6,830	8.5		3	8.8	
			1530		19.7		6,840	8.5		3	8.7	
			1530		23.0		6,840	8.5			8.7	
			1531		26.2		6,840	8.5		3 3	8.7	
			1533		29.5		6,830	8.5		3	8.7	
			1535		32.8			8.5				
			1534		36.1		6,800			1	8.7	
			1536				6,820	8.5		.1	8.7	
			1536		39.4		6,830	8.5		.2	8.7	
					42.7		6,830	8.5		.3	8.7	
			1538		45.9		6,850	8.5		.8	7.8	
			1539		49.2		6,760	8.5		1.7	4.6	

Supplement 1. Results for field-measured properties and constituents for lake and wetland sites—Continued [mm, millimeters; µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; --, no data; e, estimated]

Site number (see figure 1 for location)	Site name	Date	Time	Depth at sampling location (feet)	Measure- ment depth (feet)	Barometric pressure (mm of Hg)	Specific conduc- tance, field (µS/cm at 25°C)	pH, field (standard units)	Temper- ature, air (°C)	Temper- ature, water (°C)	Oxygen, dissolved (mg/L)	Oxygen, dissolved (percent saturation)
7	East Devils LakeContinued	08/02/01	0920	51.5	0	731	6,000	8.3	22.0	21.9	9.5	115
	Zant De la Zant Commune	00.02.01	0921		3.3		6,080	8.5		21.9	8.0	
			0922		6.6		6,080	8.5		21.9	7.8	
			0923		13.1		6,090	8.6		21.9	7.7	
			0924		19.7		6,090	8.6		21.9	7.6	
			0925		26.2		6,090	8.6		21.9	7.5	
			0926		32.8		6,080	8.6		21.9	7.5	
			0927		39.4		6,180	8.5		19.6	4.0	
			0928		45.9		6,280	8.3		16.0	.6	
			0929		51.5		6,280	8.3		15.2	.5	
			0929		31.3		0,200	0.5	77	13.2		
9	Lake Ashtabula near north end	03/13/01	1430	8.2	3.0	e722	1,350	8.5	7.0	0	5.0	
			1431		4.9		1,360	8.5		0	4.4	
			1432		6.6		1,360	8.4		0	4.3	
			1433		8.2		1,360	8.4		0	4.1	
		08/07/01	1100	8.9	0	e727	1,010	7.6	30.5	27.9	7.0	
		00/07/01	1101		3.3		1,100	7.7		27.9	6.4	
			1102		6.6		1,100	7.8		27.9	5.9	
			1103		8.9		1,100	7.8		27.7	5.7	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01	1020	18.4	2.6	722	1,560	8.6	4.5	0	11.0	80
10	Lake Ashtabula at Balulilli Dalli, North Dakota	03/13/01	1020	10.4	3.3	122	1,550	8.5	4.5	.3	10.9	
			1021		6.6		1,520	8.4		1.0	10.7	
			1022		9.8		1,520	8.2		2.0	8.1	
			1023		13.1		1,500	8.1		2.6	6.3	
			1024		16.4		1,710	8.0		3.3	2.6	
			1025		18.0		1,730	7.9		3.5	1.8	
		08/07/01	1230	27.9	0	727	1,180	8.4	34.5	26.7	11.3	149
		00/07/01	1230	27.9	3.3	121	1,180	8.4	34.3	26.7	11.3	149
			1231		6.6		1,180	8.4		25.6	9.6	-
			1232		9.8		1,180	8.3		25.5	8.2	
			1233		13.1		1,180	8.3		25.4	7.5	
			1234		16.4		1,190	8.3		25.4	6.9	
			1236		19.7		1,190	8.3		24.7	5.9	
			1237		23.0		1,190	8.3		24.4	4.9	
			1238		26.2		1,190	8.2	77	23.6	.7	
			1239		27.9		1,190	8.2		23.5	.5	

Supplement 2. Results for field-measured properties and constituents for river sites

[mm, millimeters; µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; --, no data]

Site number (see figure 1 for location)	Site name	Date	Time	Discharge (cubic feet per second)	Barometric pressure (mm of Hg)	Specific conductance, field (µS/cm at 25°C)	pH, whole water, field (standard units)	Temperature, air (°C)	Temperature, water (°C)	Turbidity, field, whole water (nephelo- metric turbidity units)	Oxygen, dissolved (mg/L)	Oxygen, dissolved (percent saturation)
2	Starkweather Coulee near	04/30/01	1140	210		808	8.2	17.5	13.5		8.3	85
	Webster, North Dakota	07/24/01	0845	55	77	711	7.6	17.5	21.8		5.5	65
8	Sheyenne River near Warwick,	04/30/01	1400	485	720	1,140	8.2	19.8	16.3	24	9.0	98
	North Dakota	07/24/01	1020	361	730	1,260	8.0	20.9	25.2	85	5.6	71
11	Sheyenne River below Baldhill	05/01/01	0830	893	717	828	8.1	17.0	8.5	14	11.0	100
	Dam, North Dakota	07/24/01	1240	382	732	1,130	8.4	20.0	24.6	20	7.4	93
12	Sheyenne River near Kindred,	05/01/01	1030	1,400	725	797	8.0	17.6	13.6	240	9.0	91
	North Dakota	07/25/01	0830	253	742	985	8.2	18.9	23.3	150	8.0	97
13	Red River of the North at Fargo,	05/01/01	1200	7,670	726	621	7.8	19.0	14.9		7.9	82
	North Dakota	07/25/01	0950	2,400	742	649	7.8	25.0	26.5	270	5.8	74
14	Red River of the North at Halstad,	05/01/01	1345	23,500	726	661	7.9	18.1	14.2		8.5	87
	Minnesota	07/25/01	1130	5,060	743	526	7.8	25.8	26.4	510	5.7	73
15	Red Lake River at Fisher,	05/01/01	1515	4,660	727	411	8.1	19.2	15.3	95	9.4	99
	Minnesota	07/25/01	1330	1,760	745	341	8.0	25.5	25.5	140	7.2	90
16	Red River of the North at	05/02/01	0730	40,000	734	531	7.9	10.0	12.8		8.7	85
	Emerson, Manitoba	07/26/01	0715	6,100	749	657	8.0	20.5	26.1	440	7.1	89

Supplement 3. Results for major-ion, trace-element, and suspended-sediment constituents for lake and wetland sites

[Samples were analyzed by the North Dakota Department of Health Laboratory; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; NS, near-surface sample collected about 3 feet above lake bottom; —, no data; μ g/L, micrograms per liter; <, less than; mm, millimeter]

Site number (see figure 1 for	Site name	Date	Time	Depth at sampling location (feet)	of sa inte	to top mple rval et)	condu (μ S /	cific ctance cm at °C)	labor (star	whole iter, ratory idard its)	disso	ium, olved as Ca)	Magno disso (mg/L a	olved
location)				, , , , , ,	NS	NB	NS	NB	NS	NB	NS	NB	NS	NB
1	Wetland site in upper Devils Lake Basin	04/30/01	1030				1,290		8.0		60		60	
		07/31/01	0715				1,900		7.2		82		90	
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	17.1	6.0	16.4	1,970	2,060	8.1	8.0	100	100	84	87
		08/01/01	1205	9.2	3.3	6.6	1,220	1,220	9.0	9.0	70	69	51	51
4	Devils Lake West Bay southwest	03/15/01	1430	12.8	10.5		2,280		8.4		90		88	
		08/01/01	1430		3.3		1,890	155	8.9		76		72	
5	Devils Lake Main Bay	03/14/01	1030	45.6	6.0	43.3	2,270	2,430	8.6	8.4	84	83	92	98
		08/01/01	0845	48.9	45.9		2,050				71		75	
6	Devils Lake East Bay	03/14/01	1330	36.4	6.6		3,640		8.5		85		140	
		08/02/01	0740	38.7	3.3		3,230		8.8		74		120	
7	East Devils Lake	03/14/01	1615	49.2	6.2	47.6	6,760	6,770	8.5	8.5	94	89	270	260
		08/02/01	0935	51.5	3.3	48.2	6,060	6,180	8.8	8.6	81	84	220	230
9	Lake Ashtabula near north end	03/13/01	1450	8.2	6.2		1,310		7.8		110		57	
		08/07/01	1105	8.9	3.3		1,120		8.0		66		48	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01	1120	18.4	6.0	15.7	1,470	1,700	8.3	8.0	110	120	72	86
		08/07/01	1240	27.9	3.3	24.6	1,190	1,190	8.6	8.5	70	71	54	54

Supplement 3. Results for major-ion, trace-element, and suspended-sediment constituents for lake and wetland sites—Continued

[Samples were analyzed by the North Dakota Department of Health Laboratory; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; NS, near-surface sample collected about 3 feet below water surface; NB, near-bottom sample collected about 3 feet above lake bottom; —, no data; μ g/L, micrograms per liter; <, less than; mm, millimeter]

Site number (see figure 1 for	Site name	Date	Time	Depth at sampling location (feet)	Depth of sa inte (fe	mple	Sodi disso (mg/L s	lved	Potass disso (mg/L	lved	pH labor	linity, ion to 4.5, ratory s CaCO ₃)	Sulf disso (mg/L a	olved
location)					NS	NB	NS	NB	NS	NB	NS	NB	NS	NB
1	Wetland site in upper Devils Lake Basin	04/30/01	1030				140		14		270		420	
		07/31/01	0715				220		16		360		700	
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	17.1	6.0	16.4	240	260	38	40	390	430	520	520
	The same services and constitute and the same services are same services are same services and the same services are s	08/01/01	1205	9.2	3.3	6.6	110	110	22	22	320	320	320	320
4	Devils Lake West Bay southwest	03/15/01	1430	12.8	10.5		290	~~	44		410		650	
		08/01/01	1430		3.3	***	230		36		390	~~	510	~-
5	Devils Lake Main Bay	03/14/01	1030	45.6	6.0	43.3	320	350	47	50	360	370	690	720
		08/01/01	0845	48.9	45.9		260		39		350		560	
6	Devils Lake East Bay	03/14/01	1330	36.4	6.6		570		76		420		1,300	
		08/02/01	0740	38.7	3.3		480		64		430		1,000	
7	East Devils Lake	03/14/01	1615	49.2	6.2	47.6	1,300	1,200	150	140	530	540	2,700	2,700
		08/02/01	0935	51.5	3.3	48.2	1,100	1,100	120	120	570	580	2,400	2,200
9	Lake Ashtabula near north end	03/13/01	1450	8.2	6.2		120		8.2		460		230	
		08/07/01	1105	8.9	3.3		120		11		340		270	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01	1120	18.4	6.0	15.7	150	180	15	15	460	550	310	370
		08/07/01	1240	27.9	3.3	24.6	120	120	11	11	390	420	280	280

Supplement 3. Results for major-ion, trace-element, and suspended-sediment constituents for lake and wetland sites—Continued

[Samples were analyzed by the North Dakota Department of Health Laboratory; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; NS, near-surface sample collected about 3 feet above lake bottom; --, no data; μ g/L, micrograms per liter; <, less than; mm, millimeter]

Site number (see figure 1 for	Site name	Date	Time	Depth at sampling location (feet)	of sa inte	to top mple erval eet)	Chlor disso (mg/L a	ved	disso sur consti	ids, blved, n of ituents g/L)	100000000000000000000000000000000000000	ole water as Fe)	whol	ganese, le water ug/L)
location)					NS	NB	NS	NB	NS	NB	NS	NB	NS	NB
1	Wetland site in upper Devils Lake Basin	04/30/01	1030				8.1		863		50		110	
		07/31/01	0715				6.5		1,330		20		160	
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	17.1	6.0	16.4	87	100	1,300	1,370	20	180	410	1,800
	•	08/01/01	1205	9.2	3.3	6.6	36	45	802	808	150	130	120	110
4	Devils Lake West Bay southwest	03/15/01	1430	12.8	10.5		130		1,540		<10		40	
	2.107-10.2070.007-10.2074	08/01/01	1430		3.3		99		1,260		210		50	
5	Devils Lake Main Bay	03/14/01	1030	45.6	6.0	43.3	120	130	1,570	1,650	10	30	<10	230
		08/01/01	0845	48.9	45.9		110		1,320	77	<10		20	
6	Devils Lake East Bay	03/14/01	1330	36.4	6.6		260		2,660		<10		<10	
	SE SENS CHECKS	08/02/01	0740	38.7	3.3		220		2,250		70	44	30	
7	East Devils Lake	03/14/01	1615	49.2	6.2	47.6	520	530	5,290	5,320	40	40	<10	10
		08/02/01	0935	51.5	3.3	48.2	490	490	4,670	4,710	<10	<10	<10	320
9	Lake Ashtabula near north end	03/13/01	1450	8.2	6.2		17		830		210		540	
		08/07/01	1105	8.9	3.3		12		727		220		160	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01	1120	18.4	6.0	15.7	22	28	954	1,140	110	50	320	1,100
		08/07/01	1240	27.9	3.3	24.6	17	17	789	809	10	< 10	130	310

Supplement 3. Results for major-ion, trace-element, and suspended-sediment constituents for lake and wetland sites—Continued

[Samples were analyzed by the North Dakota Department of Health Laboratory; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; NS, near-surface sample collected about 3 feet above lake bottom; --, no data; μ g/L, micrograms per liter; <, less than; mm, millimeter]

Site number (see figure 1	Site name	Date	Time	Depth of lake at sampling location	of sa inte	to top mple erval eet)	sedi	ended ment g/L)	sedi (perce	ended ment nt finer 062 mm)
for location)				(feet)	NS	NB	NS	NB	NS	NB
1	Wetland site in upper Devils Lake Basin	04/30/01	1030				4		91	
		07/31/01	0715	77			31		97	
3	Devils Lake West Bay near Pelican Lake	03/15/01	1155	17.1	6.0	16.4				
		08/01/01	1205	9.2	3.3	6.6	23	31	98	95
4	Devils Lake West Bay southwest	03/15/01	1430	12.8	10.5					
		08/01/01	1430		3.3		10		98	
5	Devils Lake Main Bay	03/14/01	1030	45.6	6.0	43.3	2	3	91	96
		08/01/01	0845	48.9	45.9		2		88	
6	Devils Lake East Bay	03/14/01	1330	36.4	6.6		1		85	122
		08/02/01	0740	38.7	3.3		5		92	
7	East Devils Lake	03/14/01	1615	49.2	6.2	47.6	4		99	
		08/02/01	0935	51.5	3.3	48.2	29	154	100	100
9	Lake Ashtabula near north end	03/13/01	1450	8.2	6.2					
		08/07/01	1105	8.9	3.3		8	44	88	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01	1120	18.4	6.0	15.7	3	23	92	97
		08/07/01	1240	27.9	3.3	24.6	3	4	79	86

Supplement 4. Results for major-ion, trace-element, and suspended-sediment constituents for river sites

[Samples were analyzed by the North Dakota Department of Health Laboratory; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; --, no data; <, less than; μ g/L, micrograms per liter; mm, millimeters; M, presence verified, not quantified]

Site number (see figure 1 for location)	Site name	Date	Time	Specific conductance (µS/cm at 25°C)	pH, whole water, laboratory (standard units)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)	Potassium, dissolved (mg/L as K)	Alkalinity, titration to pH 4.5, laboratory (mg/L as CaCO ₃)
2	Starkweather Coulee near Webster, North Dakota	04/30/01	1140	816	8.3	80	38	36	19	200
		07/24/01	0845			76	42	59	13	170
8	Sheyenne River near Warwick, North Dakota	04/30/01	1400	1,140	8.4	63	52	120	11	360
		07/24/01	1020	1,280	7.9	59	52	160	12	320
11	Sheyenne River below Baldhill Dam, North Dakota	05/01/01	0830	838	8.2	56	35	73	10	230
		07/24/01	1240	1,150	8.4	74	55	120	12	310
12	Sheyenne River near Kindred, North Dakota	05/01/01	1030	793	8.2	64	32	60	10	230
		07/25/01	0830	993	7.8	88	46	79	11	250
13	Red River of the North at Fargo, North Dakota	05/01/01	1200	626	7.6	62	32	19	7.6	140
		07/25/01	0950	662	7.0	66	41	20	7.0	160
14	Red River of the North at Halstad, Minnesota	05/01/01	1345	672	7.9	68	35	24	8.2	170
		07/25/01	1130	680		80	44	26	9.2	210
15	Red Lake River at Fisher, Minnesota	05/01/01	1515	419	8.0	62	22	<3.0	4.3	160
		07/25/01	1330			49	17	3.0	2.9	150
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	539	7.8	56	25	18	8.2	150
		Replicate	0740	536	7.8	56	24	18	7.9	150
		07/26/01	0715	665	7.0	61	33	26	5.9	160
		Replicate	0725							

Supplement 4. Results for major-ion, trace-element, and suspended-sediment constituents for river sites—Continued

[Samples were analyzed by the North Dakota Department of Health Laboratory; μ S/cm, microsiemens per centimeter; $^{\circ}$ C, degrees Celsius; mg/L, milligrams per liter; --, no data; <, less than; μ g/L, micrograms per liter; mm, millimeters; M, presence verified, not quantified]

Site number (see figure 1 for location)	Station name	Date	Time	Sulfate, dissolved (mg/L as SO ₄)	Chloride, dissolved (mg/L as CI)	Solids, dissolved, sum of constituents (mg/L)	Iron, whole water (mg/L as Fe)	Manganese, whole water (μg/L)	Suspended sediment (mg/L)	Suspended sediment (percent finer than 0.062 mm)
2	Starkweather Coulee near Webster, North Dakota	04/30/01	1140	210	24	524	2,900	740	394	100
		07/24/01	0845	290	28	616	M	M	6	96
8	Sheyenne River near Warwick, North Dakota	04/30/01	1400	270	15	747	600	100	21	98
		07/24/01	1020	290	15	786	M	M	95	99
11	Sheyenne River below Baldhill Dam, North Dakota	05/01/01	0830	200	12	524	350	330	17	90
		07/24/01	1240	270	14	734	M	M	17	95
12	Sheyenne River near Kindred, North Dakota	05/01/01	1030	190	15	511	2,500	420	166	84
		07/25/01	0830	220	19	622	4,100	570	211	96
13	Red River of the North at Fargo, North Dakota	05/01/01	1200	180	10	393	2,200	80	138	100
		07/25/01	0950	160	11	400	M	M	278	100
14	Red River of the North at Halstad, Minnesota	05/01/01	1345	170	12	425	3,400	130		
		07/25/01	1130	150	14	456	12,500	M	499	100
15	Red Lake River at Fisher, Minnesota	05/01/01	1515	50	5.4	244	2,900	130	133	95
		07/25/01	1330	15	3.0	183	M	M	116	98
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	110	12	317	M	M	~~	
		Replicate	0740	110	.4	308	3,800	130	302	100
		07/26/01	0715	130	20	372	10	M	419	100
		Replicate	0725							100

Supplement 5. Results for mercury and organic-carbon constituents for lake and wetland sites

[Samples were analyzed by the U.S. Geological Survey Wisconsin District Mercury Laboratory; ng/L, nanograms per liter; NS, near-surface sample collected about 3 feet below water surface; NB, near-bottom sample collected about 3 feet above lake bottom; --, no data; <-, less than; mg/L, milligrams per liter]

Site number (see figure 1 for location)	Site name	Date	Time		Methylmercury, dissolved (ng/L)		Methylmercury, particulate (ng/L)		Methylmercury, whole water (ng/L)		Total mercury, dissolved (ng/L)	
			NS	NB	NS	NB	NS	NB	NS	NB	NS	NB
1	Wetland site in upper Devils Lake Basin	04/30/01 07/31/01	1030 0715		0.35 3.13		0.04		0.39 3.53		1.29 5.31	
3	Devils Lake West Bay near Pelican Lake	03/15/01 08/01/01	1155 Replicate 1205	1225 1210	<.04 <.04 <.04	0.22 .06	<.02 <.02 .21	<0.02 .20	<.04 <.04 .21	0.22	.50 1.43 1.22	0.86
4	Devils Lake West Bay southwest	03/15/01 08/01/01	1400 1430	1430	<.04 <.04	<.04	<.02	.02	<.04	<.04	.34 .79	.37
5	Devils Lake Main Bay	03/14/01 08/01/01	1030 0840	1100 0845	<.04	<.04	<.02	<.02 .04	<.04	<.04	.40 .79	.38 .58
6	Devils Lake East Bay	03/14/01 08/02/01 08/02/01	1330 0740 Replicate		<.04 .10 .13		<.02 .10 .09		<.04 .20 .21		.41 .85 .97	
7	East Devils Lake	03/14/01 08/02/01	1615 0935	1645 0940	<.04 <.04	<.04 .26	<.02	<.02 .07	<.04 <.04	<.04 .34	.63 .80	.64 1.25
9	Lake Ashtabula near north end	03/13/01 08/07/01	1450 1105		.06 .37		<.02		.06 .46		.53 2.07	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01 08/07/01	1120 1240	1150 1245	<.04	.22 .21	<.02	<.02 .05	<.04 .28	.22 .27	.63 .64	.88 .68

Supplement 5. Results for mercury and organic-carbon constituents for lake and wetland sites—Continued

[Samples were analyzed by the U.S. Geological Survey Wisconsin District Mercury Laboratory; ng/L, nanograms per liter; NS, near-surface sample collected about 3 feet below water surface; NB, near-bottom sample collected about 3 feet above lake bottom; --, no data; <, less than; mg/L, milligrams per liter]

Site number (see figure 1 for location)	Site name	Date	Time		Total mercury, particulate (ng/L)		Total mercury, whole water (ng/L)		Organic carbon, dissolved (mg/L)		Organic carbon, whole water (mg/L)	
			NS	NB	NS	NB	NS	NB	NS	NB	NS	NB
1	Wetland site in upper Devils Lake Basin	04/30/01 07/31/01	1030 0715		0.14 1.71		1.43 7.02		19.9 30.7		18.7 31.0	
3	Devils Lake West Bay near Pelican Lake	03/15/01 03/15/01 08/01/01	1155 Replicate 1205	1225 1210	<.02 <.02 1.76	0.03 .92	.50 1.43 2.98	0.89	20.7 20.7 14.7	21.7 14.7	21.0 21.2 15.4	20.7 15.7
4	Devils Lake West Bay southwest	03/15/01 08/01/01	1400 1430	1430	.04 1.07	.22	.38 1.86	.59	19.3 17.2	19.0	20.0 17.9	19.5
5	Devils Lake Main Bay	03/14/01 08/01/01	1030 0840	1100 0845	<.02	<.02 .28	.40 1.11	.38 .86	18.0 14.1	18.7 14.6	17.9 14.1	18.2 14.7
6	Devils Lake East Bay	03/14/01 08/02/01 08/02/01	1330 0740 Replicate		<.02 .34 .45		.41 1.20 1.41		24.3 19.2 20.0		24.2 19.6 19.8	
7	East Devils Lake	03/14/01 08/02/01	1615 0935	1645 0940	.07	<.02 .48	.70	.64 1.73	32.5 27.6	32.5 27.4	32.2 27.8	32.9 27.3
9	Lake Ashtabula near north end	03/13/01 08/07/01	1450 1105		.55 1.04		1.08 3.11	2	8.7 18.6		8.5 18.1	
10	Lake Ashtabula at Baldhill Dam, North Dakota	03/13/01 08/07/01	1120 1240	1150 1245	<.02	<.02 .25	.63 .96	.88 .93	18.0 14.4	18.1 14.2	17.8 14.9	18.9 14.0

Supplement 6. Results for mercury and organic-carbon constituents for river sites

[Samples were analyzed by the U.S. Geological Survey Wisconsin District Mercury Laboratory; ft³/s, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter; --, no data]

Site number (see figure 1 for ocation)	Site name	Date	Time	Discharge (ft ³ /s)	Methyl- mercury, dissolved (ng/L)	Methyl- mercury, particu- late (ng/L)	Methyl- mercury, whole water (ng/L)	Total mercury, dissolved (ng/L)	Total mercury, particu- late (ng/L)	Total mercury, whole water (ng/L)	Organic carbon, dis- solved (mg/L)	Organic carbon, whole water (mg/L)
2	Starkweather Coulee near Webster, North Dakota	04/30/01	1140	220	0.21	0.25	0.45	2.11	4.22	6.33	13.7	13.1
		07/24/01	0845	56	.96	.17	1.13	2.57	.66	3.22	15.4	15.9
8	Sheyenne River near Warwick, North Dakota	04/30/01	1400	460	.19	.08	.27	1.31	1.11	2.42	14.1	13.1
		07/24/01	1020	380	.13	.08	.21	2.32	3.53	5.85	21.3	20.9
11	Sheyenne River below Baldhill Dam, North Dakota	05/01/01	0830	720	.09	.12	.20	1.59	.97	2.56	11.2	10.8
	•	07/24/01	1240	370	.18	.09	.27	.96	1.04	2.00	13.8	13.6
12	Sheyenne River near Kindred, North Dakota	05/01/01	1030	1,650	.08	.21	.29	1.60	16.25	17.84	8.7	8.8
		07/25/01	0830	290	.47	.97	1.44	1.57	11.55	13.12	9.4	9.7
13	Red River of the North at Fargo, North Dakota	05/01/01	1200	7,700	.06	.14	.20	1.39	6.41	7.81	7.9	7.6
	7.00 to 10.00 to 10.0	07/25/01	0950	2,880	.13	.35	.47	.95	15.31	16.27	9.1	9.3
14	Red River of the North at Halstad, Minnesota	05/01/01	1345	23,500	.08	.17	.25	1.54	11.49	13.04	8.4	8.1
		07/25/01	1130	5,050	.07	.39	.46	1.09	25.81	26.90	8.2	7.9
15	Red Lake River at Fisher, Minnesota	05/01/01	1515	4,660	.11	.12	.23	1.32	4.41	5.73	11.6	11.2
		07/25/01	1330	1,760	.29	.16	.45	1.56	4.30	5.86	15.6	15.8
16	Red River of the North at Emerson, Manitoba	05/02/01	0730	40,000	.06	.10	.16	1.91	7.49	9.40	8.5	8.4
		05/02/01	Replicate		.07	.09	.15	1.78	7.31	9.09	8.9	8.8
		07/26/01	0715	6,100	.06	.31	.37	1.13	21.30	22.43	9.4	9.4
		07/26/01	Replicate		.07	.34	.41	1.06	22.49	23.55	9.4	9.3



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