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# Characteristics of Water, Sediment, and Benthic Communities of the Wolf River, Menominee Indian Reservation, Wisconsin, Water Years 1986–98

Water-Resources Investigations Report 01–4019



Prepared in cooperation with the  
Menominee Indian Tribe of Wisconsin



# CHARACTERISTICS OF WATER, SEDIMENT, AND BENTHIC COMMUNITIES OF THE WOLF RIVER, MENOMINEE INDIAN RESERVATION, WISCONSIN, WATER YEARS 1986–98

By Herbert S. Garn, Barbara C. Scudder,  
Kevin D. Richards, and Daniel J. Sullivan

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U.S. GEOLOGICAL SURVEY  
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MENOMINEE INDIAN TRIBE OF WISCONSIN

Middleton, Wisconsin  
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**U.S. DEPARTMENT OF THE INTERIOR**  
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## CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To Obtain
millimeter (mm)	0.0394	inch
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
meter (m)	3.281	foot
square meter (m <sup>2</sup> )	10.76	square foot
mile (mi)	1.609	kilometer
square mile (mi <sup>2</sup> )	2.590	square kilometer
square centimeter (cm <sup>2</sup> )	0.1550	square inch

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:  

$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32.$$

**Vertical Datum:** In this report “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level of both the United States and Canada, formerly called Sea Level Datum of 1929.

**Water year:** Water year is defined as the period beginning October 1 and ending September 30, designated by the calendar year in which it ends.

**Abbreviated water-quality units used in this report:** Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (µg/L), or nanogram per liter (ng/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Other units of measurement used in this report are microsiemens per centimeter at 25° Celsius (µS/cm), number of algal cells per square centimeter (cell/cm<sup>2</sup>), and resistance given in megaohms (Mohm).

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

### Other Abbreviations Used in this Report:

MCL	Maximum Contaminant Level
MDL	Minimum Detection Limit
MRL	Method Reporting Level
MTV	Mean Tolerance Value
NAWQA	National Water-Quality Assessment Program
NWQL	National Water-Quality Laboratory, U.S. Geological Survey



# Characteristics of Water, Sediment, and Benthic Communities of the Wolf River, Menominee Indian Reservation, Wisconsin, Water Years 1986–98

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## Abstract

Analyses and interpretation of water quality, sediment, and biological data from water years 1986 through 1998 indicated that land use and other human activities have had only minimal effects on water quality in the Wolf River upstream from and within the Menominee Indian Reservation in northeastern Wisconsin. Relatively high concentrations of calcium and magnesium (natural hardness), iron, manganese, and aluminum were measured in Wolf River water samples during water years 1986–98 from the three sampled sites and attributed to presence of highly mineralized geologic materials in the basin. Average calcium and magnesium concentrations varied from 22–26 milligrams per liter (mg/L) and 11–13 mg/L, respectively. Average iron concentrations ranged from 290–380 micrograms per liter ( $\mu\text{g/L}$ ); average manganese concentrations ranged from 53–56 mg/L. Average aluminum concentrations ranged from 63–67  $\mu\text{g/L}$ . Mercury was present in water samples but concentrations were not at levels of concern. Levels of Kjeldahl nitrogen, ammonia, nitrite plus nitrate, total phosphorus, and orthophosphorus in water samples were often low or below detection limits (0.01–0.10 mg/L). Trace amounts of atrazine (maximum concentration of 0.031  $\mu\text{g/L}$ ), deethylatrazine (maximum 0.032  $\mu\text{g/L}$ ), and alachlor (maximum of 0.002  $\mu\text{g/L}$ ) were detected. Low concentrations of most trace elements were found in streambed sediment.

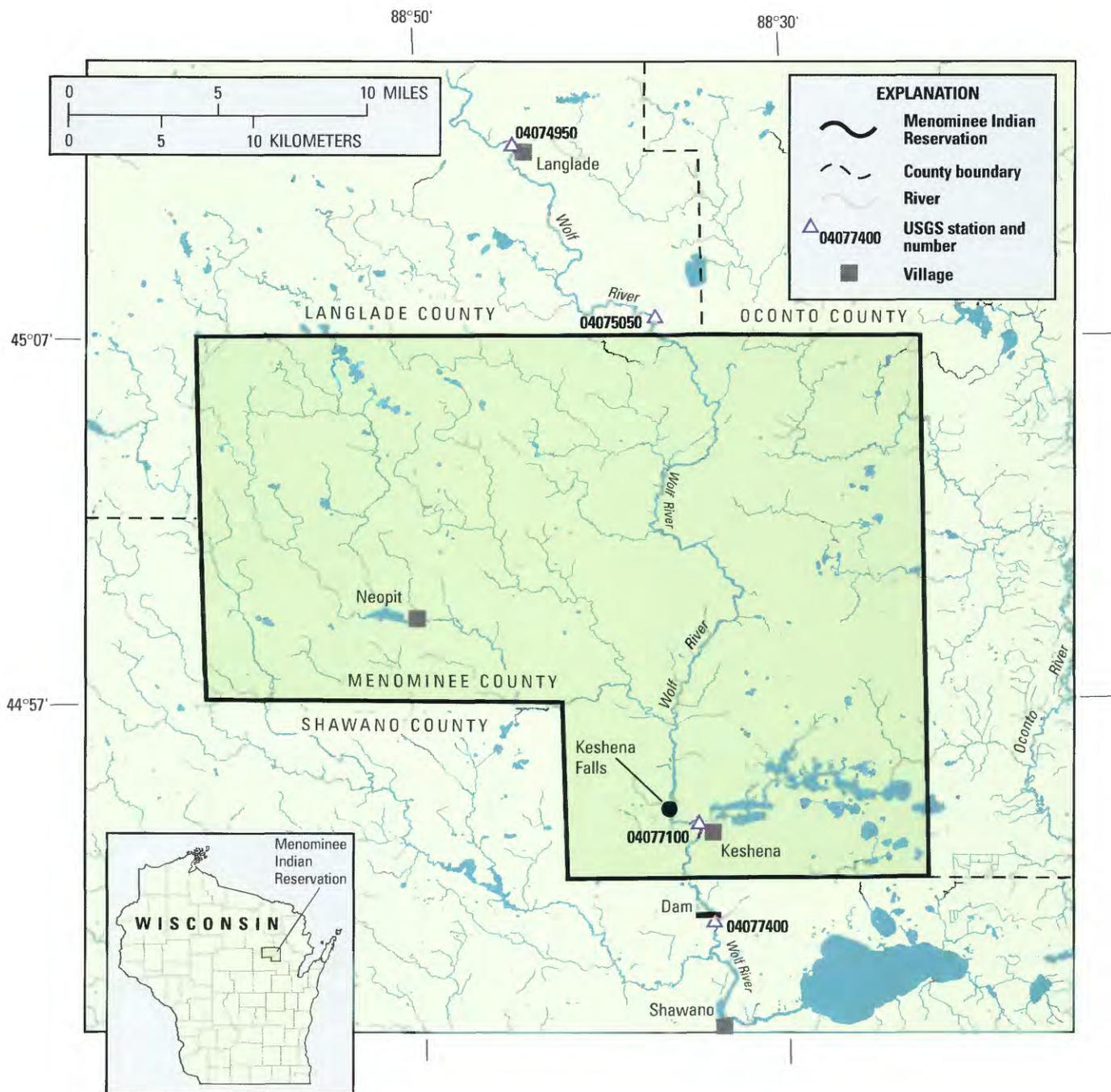
Tissues of fish and aquatic invertebrates collected once each year from 1995 through 1998 at the Langlade and Keshena sites, near the northern and southern boundaries of the Reservation,

respectively, were low in concentrations of most trace elements. Arsenic and silver in fish livers from both sites were less than or equal to 2  $\mu\text{g/g}$  arsenic and less than 1  $\mu\text{g/g}$  silver for dry weight analysis, and concentrations of antimony, beryllium, cadmium, cobalt, lead, nickel, and uranium were all below detection limits (less than 1  $\mu\text{g/g}$  dry weight). Concentrations of most other trace elements in fish were low, with the exceptions of chromium, copper, mercury, and selenium; however, these concentrations are not at levels of concern. Concentrations of all trace elements analyzed in whole caddisfly larvae also were low compared to those reported in the literature.

During 1998, a total of 48 species of macroinvertebrates were identified at each of two sampled sites, with similar numbers of genera represented at both: 41 at Keshena and 44 at Langlade. The percentage EPT (Ephemeroptera, Plecoptera, and Trichoptera) was 52 at Keshena and 77 at Langlade; these relatively large percentages suggest very good to excellent water quality at these sites. A total of 52 algal taxa were identified at the Wolf River near Langlade. Diatoms made up 96 percent of the algal biomass. A total of 58 algal taxa were identified at Keshena, including 48 diatom taxa (83 percent). Although diatoms accounted for just 22 percent of the algal relative abundance, in cells per square centimeter, diatoms contributed 91 percent of the total algal biomass. The overall biological integrity of the Keshena and Langlade sites, based on diversity, siltation, and pollution indexes for diatoms is excellent.

## INTRODUCTION

The Menominee Indian Reservation constitutes Menominee County in northern Wisconsin (fig. 1).



**Figure 1.** Study area, location of streamflow-gaging and data-collection stations 04075050 at Highway M near Langlade, 04077100 at Keshena, and 04077400 near Shawano, Menominee Indian Reservation, Wisconsin.

Maintaining the quality and pristine nature of rivers and ground water on the Reservation is extremely important to the Menominee Indian Tribe. Tribal Ordinances have been established to protect the integrity of the Reservation waters. Additionally, the Wolf River is a Congressionally-designated Wild and Scenic River from the northern boundary of the Reservation to Keshena Falls. For these reasons, the U.S. Geological Survey (USGS), in cooperation with the Menominee Indian Tribe of Wisconsin, conducted a detailed assessment of the quality of streamwater on the reservation, including analysis of sediment and selected aquatic organisms. A description of general surface- and ground-water quality on the Menominee Indian Reservation was previously published in Krohelski and others (1994).

## Purpose and Scope

This report documents the quality of water, sediment, and selected biological organisms in the Wolf River from water year 1986 through water year 1998 within and near the north and south boundaries of the Menominee Indian Reservation (fig. 1). Data contained in this report, along with the referenced data and reports, provide a historical data base from which any substantial future changes may be determined in water-quality, sediment composition and quality, and biological organism health and species diversity in the Wolf River within the Menominee Reservation boundaries.

Specific objectives for this report are the following:

1. Use discharge and water-quality data collected at Highway M near Langlade, Keshena, and Shawano from 1986 through 1998 to describe and document the current condition of the Wolf River, its bottom sediments, and biota within the boundaries of the Menominee Indian Reservation.
2. Document the baseline water quality of the Wolf River at the northern boundary where it enters the Reservation and at the southern boundary where it leaves the Reservation.
3. Document concentrations of a broad suite of trace elements and pesticides in water-column samples.
4. Document particle-size fractions and associated trace-element concentrations of the fine streambed sediments at Langlade and Keshena.

5. Document concentrations of specific trace elements in composite samples of fish livers and caddisfly larvae, and to determine biological indexes of water quality at Langlade and Keshena.

## Description of the Study Area

The Menominee Indian Reservation occupies all of Menominee County, Wisconsin, an area of approximately 346 mi<sup>2</sup> in northeastern Wisconsin (fig. 1). The Wolf River flows south through the Reservation. The Wolf River and its tributaries drain all but the eastern quarter of the Reservation, which is drained by the Oconto River.

The Reservation is underlain by igneous and metamorphic bedrock that is buried beneath loamy and sandy gravelly surficial deposits (Sullivan, 1995). Average annual precipitation is approximately 30 in. Land surface elevations on the Reservation range from 1,400 ft above sea level in the northwest to 800 ft in the southeast. The population of the Reservation is approximately 3,890 (U.S. Army Corps of Engineers, 1995).

The Shawano hydroelectric plant has a dam on the Wolf River near Shawano (near USGS streamgaging station 04077400), approximately 3,700 ft downstream from the Fairgrounds Road Bridge in Keshena. The remnants of the Keshena Falls Dam still remain just upstream from the town of Keshena. Ice-jam-induced flooding has increased in frequency since this dam failed in 1972 (U.S. Army Corps of Engineers, 1995).

Land-use data in table 1 are based on the Wolf River drainage basin above the Shawano Dam to the headwaters. The Level I land-use summary contains the broadest categorizations, and Levels II and III illustrate the same data in component subcategories. Forest is the principal land-use category; 71 percent of the basin above the Shawano Dam is forested, whereas 93 percent of the Menominee Indian Reservation is forested. Lumbering is the major industry on the Reservation and it is closely monitored by the Tribe. The next largest land-use category is wetlands, encompassing 15 percent of the basin. A small percentage (<5) of land use in the drainage basin outside the Reservation is agriculture; most of this use is for hay fields, although small acreages of row crops and cranberries are cultivated.

Land-use-related activities in the Wolf River Basin, both upstream from and on the Menominee Reservation, may influence the water quality of the Wolf River

**Table 1.** Wisconsin Initiative for Statewide Cooperation on Landscape Analysis and Data (WISCLAND) land use/land cover for the Wolf River near Shawano, Wis. (USGS station 04077400)

[Data from Lillesand and others, 1998; CRP, set-aside land in Conservation Reserve Program; mi<sup>2</sup>, square mile]

<b>WISCLAND Land use/land cover for the Wolf River near Shawano, WI (04077400)</b>			
<b>Land Use description, level I</b>	<b>Grid-code</b>	<b>Sum of areas (mi<sup>2</sup>)</b>	<b>Percent of total area</b>
Urban/developed	100–109	1.62	0.195
Agriculture	110–148	36.20	4.369
Grassland	150	34.13	4.119
Forest	160–190	592.41	71.493
Open water	200	27.77	3.351
Wetland	210–234	126.66	15.286
Barren	240	5.45	.658
Shrubland	250	4.37	.527
		828.62	100.000
<b>Land Use description, level II</b>	<b>Grid-code</b>	<b>Sum of areas (mi<sup>2</sup>)</b>	<b>Percent of total area</b>
Urban: High intensity	101	0.39	0.048
Urban: Low intensity	104	1.22	.148
Agriculture: Crops	111–124	35.96	4.340
Agriculture: Cranberry bog	148	.24	.029
Grassland (including timothy, rye, pasture, idle, CRP, grass, and volunteer)	150	34.13	4.119
Forest: Coniferous	161–173	36.88	4.451
Forest: Broad-leaved deciduous	175–187	463.46	55.931
Forest: Mixed deciduous/coniferous	190	92.07	11.111
Open water	200	27.77	3.351
Wetland: Emergent/wet meadow	211–212	7.47	.901
Wetland: Lowland shrub	217–220	28.02	3.382
Wetland: Forested	222–234	91.17	11.003
Barren	240	5.45	.658
Shrubland	250	4.37	.527
		828.62	100.000
<b>Land Use description, level III</b>	<b>Grid-code</b>	<b>Sum of areas (mi<sup>2</sup>)</b>	<b>Percent of total area</b>
Urban: High intensity	101	0.39	0.048
Urban: Low intensity	104	1.22	.148
Agriculture: Herbaceous/field crops	111	21.84	2.636
Agriculture: Herbaceous/field crops, corn	113	1.03	.125

**Table 1.** Wisconsin Initiative for Statewide Cooperation on Landscape Analysis and Data (WISCLAND) land use/land cover for the Wolf River near Shawano, Wis. (USGS station 04077400)—Continued

[Data from Lillesand and others, 1998; CRP, set-aside land in Conservation Reserve Program; mi<sup>2</sup>, square mile]

<b>WISCLAND Land use/land cover for the Wolf River near Shawano, WI (04077400)</b>			
<b>Land Use description, level III</b>	<b>Grid-code</b>	<b>Sum of areas (mi<sup>2</sup>)</b>	<b>Percent of total area</b>
Agriculture: Herbaceous/field crops, other row crops	118	1.00	.121
Agriculture: Herbaceous/field crops, forage crops (includes hay and hay/mix)	124	12.08	1.458
Agriculture: Cranberry bog	148	.24	.029
Grassland (including timothy, rye, pasture, idle, CRP, grass, and volunteer)	150	34.13	4.119
Forest: Coniferous, jack pine	162	5.39	.651
<b>Land Use description, level III</b>	<b>Grid-code</b>	<b>Sum of areas (mi<sup>2</sup>)</b>	<b>Percent of total area</b>
Forest: Coniferous, red pine	163	15.98	1.928
Forest: Coniferous, white spruce	166	1.35	.162
Forest: Coniferous, mixed/other coniferous	173	14.17	1.710
Forest: Broad-leaved deciduous, aspen	176	86.89	10.486
Forest: Broad-leaved deciduous, oak	177	6.95	.839
Forest: Broad-leaved deciduous, red oak	180	.11	.013
Forest: Broad-leaved deciduous, maple	183	81.33	9.816
Forest: Broad-leaved deciduous, sugar maple	185	31.05	3.748
Forest: Broad-leaved deciduous, mixed/other broad-leaved deciduous	187	257.13	31.031
Forest: Mixed deciduous/coniferous	190	92.07	11.111
Open water	200	27.77	3.351
Wetland: Emergent/wet meadow	211	7.47	.901
Wetland: Lowland shrub	217	5.88	.710
Wetland: Lowland shrub, broad-leaved deciduous	218	14.63	1.766
Wetland: Lowland shrub, broad-leaved evergreen	219	2.87	.346
Wetland: Lowland shrub, needle-leaved	220	4.64	.560
Wetland: Forested, broad-leaved deciduous	223	13.43	1.621
Wetland: Forested, coniferous	229	39.96	4.822
Wetland: Forested, mixed deciduous/coniferous	234	37.78	4.560
Barren	240	5.45	.658
Shrubland	250	4.37	.527
		828.62	100.000

within the Reservation. Examples of environmental factors and land-use activities that could affect water quality in the Wolf River include geology and soils; atmospheric deposition of contaminants; agricultural activities, including fertilizer and pesticide applications and water withdrawals for irrigation; forestry; recreation; impoundments; road construction; wetland drainage; urban development; wastewater treatment, and potential development of a large-scale copper/zinc mine in the headwaters of the Wolf River.

## Acknowledgments

The authors gratefully acknowledge the project assistance and report review provided by Doug Cox (Menominee Indian Tribe—Environmental Department). We also are indebted to Morgan Schmidt and Brett Esser of the USGS, Jeremy Pyatskowitz and Heather Arthur (Menominee Indian Tribe—Environmental Department), and John Koss (formerly of the Menominee Indian Tribe—Environmental Department) for assistance with field collection of streambed sediment and biota. David W. Hall (USGS) assisted in report preparation; John F. Elder and David C. Heimann (USGS) also provided helpful review comments.

## METHODS OF DATA COLLECTION AND ANALYSIS

### Water Quality and Discharge Data

Stream discharge data discussed in this report were collected from water year 1986 through water year 1998

at two USGS long-term streamflow-gaging stations: 04074950, Wolf River at Langlade, Wis., about 5 mi upstream from where the river enters the Reservation at the northern boundary; and 04077400, Wolf River at Shawano, 350 ft downstream from the hydroelectric dam and below the southern boundary where the Wolf River leaves the Reservation (fig. 1). Water-quality and biological data for this project were collected on the Wolf River from water years 1986–98 at Langlade, Highway M, Keshena, and Shawano (table 2 and figure 2).

Specific biological sample collection locations on the Wolf River were (a) 1.1 miles downstream of the USGS water-quality site and County Highway M bridge near Langlade, and (b) by the State Highway 47 bridge about 1 mile upstream from the water-quality site at Keshena (fish were from the upper reach downstream from Keshena Falls to sediment reach; sediment and invertebrates were from the lower reach upstream from the medical center).

Quality-assurance procedures for water-quality monitoring are described in the USGS Quality Assurance Project Plan (QAPP), “Trace element monitoring of the Wolf River in and adjacent to the Menominee Indian Reservation, Wisconsin,” (unpublished report on file at Middleton, Wis., office of the USGS) that received required approval by the U.S. Environmental Protection Agency (USEPA) in September 1996.

Discharge and water-quality from this project are stored in the USGS National Water Information System ADAPS and QWDATA data bases. Additional historical discharge and water-quality data collected on or adjacent to the Menominee Reservation are available in the USGS ADAPS and QWDATA data bases; availabil-

**Table 2.** Description of data-collection stations for data discussed in this report

USGS station number	Station description	Parameters discussed in this report	Time period of data discussed in this report
04074950	Wolf River at Langlade	Discharge	October 1985–September 1998
04075050	Wolf River at Highway M near Langlade	Inorganics, trace elements, and pesticides in water; trace elements in sediment; trace elements in tissue	April 1986–September 1998
04077100	Wolf River at Keshena	Inorganics, trace elements, and pesticides in water; trace elements in sediment; trace elements in tissue	May 1995–September 1998
04077400	Wolf River near Shawano	Discharge; inorganics and trace elements in water	Discharge: October 1985–September 1998  Water quality: October 1989–September 1996

**A**



**B**



**Figure 2.** (A) Wolf River downstream from Highway M near Langlade; and (B) Wolf River at Keshena.

ity is summarized in table 3. Streamflow and water-quality data were previously published in the USGS annual report series “Water Resources Data—Wisconsin” for each water year.

Systematic streamflow gaging began on the Wolf River near Shawano in 1907; however, water quality was not monitored on the Reservation until the 1970’s when temperature, specific conductance, and sediment-concentration data were collected at Keshena Falls. During the 1980’s, the potential importance of trace elements in Wolf River water was recognized, and a limited sampling of trace elements was done at Langlade in the early 1980’s. Samples of water, sediment, and biota collected at Highway M near Langlade, Highway VV (Kittecon Bridge) at Keshena, and samples of water collected near Shawano during water years 1986–98 were analyzed for a more complete suite of trace metals, nutrients and pesticides. The results of those analyses are the subject of this report.

### Data Collection

Water was sampled according to protocols developed by the USGS National Water Quality Assessment (NAWQA) program (Shelton, 1994). Water-quality sampling intervals varied during the study from monthly to seasonally plus high-flow sampling. All

sites were usually sampled the same day, beginning with the most upstream site and proceeding downstream. Sample collection and processing procedures included the use of multi-vertical, depth-integrating sampling, and the use of protocols to produce contaminant-free trace-element data. Field analyses included those for pH, specific conductance, dissolved oxygen, and water temperature as measured using a multiparameter water-quality instrument that was calibrated in the field before use, according to standard procedures. Field quality control practices included obtaining at least one field blank per site per year for analysis. Strict chain-of-custody procedures were followed from the time of sample collection and internally through the laboratory until sample disposal.

### Laboratory Analyses

USGS National Water Quality Laboratory (NWQL) analytical schedules 2701 (major ions plus total suspended solids and dissolved organic carbon) schedule 1056 for total and dissolved cyanide and chemical oxygen demand, and schedule 878 (nutrients) were used during the study (appendixes 1 and 2). The minimum reporting level (MRL) is the smallest measured concentration of a constituent that may be reliably reported by the use of a given analytical method. The

**Table 3.** Discharge and water-quality data that are in U.S. Geological Survey ADAPS and QWDATA data bases from the Wolf River near the Menominee Indian Reservation

Station number, name	Drainage area, in square miles	Data type	Period of record (water years)
04074950 Wolf River at Langlade	463	Discharge Water quality (limited, but included some trace elements)	1966–98 1981–86
04075050 Wolf River at Highway M near Langlade	489	Water quality Sediment quality Biological data	1986–98
04077000 Wolf River at Keshena Falls	Not determined	Water quality (limited to temperature, specific conductance, sediment concentration)	1973, 1975, 1981–84
04077100 Wolf River at Highway VV (Kittecon Bridge) at Keshena	Not determined	Water quality Sediment quality Biological data	1995–98
04077400 Wolf River near Shawano	816	Discharge Water quality Sediment quality Biological data	1907–09, 1910–present 1989–96

method detection limit (MDL) of an analyte is the minimum concentration that can be measured and reported with 99-percent confidence that the concentration is greater than zero (Oblinger Childress and others, 1999).

A problem with incomplete digestion of phosphorus samples was discovered by the NWQL (U.S. Geological Survey Office of Water Quality Technical Memorandum 92.10, July 13, 1992) that resulted in a negative bias of historical phosphorus data collected after 1973 to September 1991. The problem was partially corrected in May 1990 and finally corrected in October 1991 with a new digestion procedure that eliminated the bias. Care must be used when interpreting phosphorus data (both total and dissolved forms) across the time boundaries of May 1990 and October 1991 because this change may have resulted in an artificial upward trend in the data.

For trace elements, NWQL schedules 2215 (USEPA drinking water total trace elements) and 1057 (whole-water recoverable and dissolved trace elements) were used for laboratory analyses (appendix 3). Low-level mercury analyses during 1996–98 (method detection limit of less than 0.1 ng/L) were done in the USGS Wisconsin District mercury laboratory. Hexavalent chromium, dissolved (MRL = 1.0 µg/L), was added to the NWQL analyses in 1997 and later that year was replaced by a Hach field test (Method no. 8023, at 10 µg/L) when the laboratory test was discontinued. Schedule 1057 consisted of a combination of GFAA (graphite furnace atomic absorption) and ICP (inductively coupled plasma) analyses. In December 1997, almost all of the dissolved-trace-element GFAA analyses (except for chromium) were replaced with the ICP/MS (inductively coupled plasma/mass spectrometry) method to improve efficiency and provide lower method detection limits.

A broad-spectrum, low-level pesticide schedule (2001) was used initially to determine the occurrence and distribution of organic pesticides in the Wolf River (appendix 4). The method detection limits for schedule 2001 were revised in 1996 (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 96–06, April 15, 1996). Schedule 2001 was replaced with a more specific schedule, 1379, for organonitrogen pesticides (triazines) in March 1997 (appendix 5).

## Data Analyses

Statistical measures used in analysis of water-quality data included reporting numbers of samples and minimum, median, and maximum values. Percentiles were computed by use of Water-Quality System (QWDATA) software of the National Water Information System (Maddy and others, 1990). In general, a statistical summary for a constituent was not generated if fewer than five observations were above the detection limit. The concentrations of a constituent in more than 50 percent of the samples need to be above the detection limit to compute a meaningful median, and greater than 75 percent of the samples need to be above the detection limit to compute meaningful 25th and 75th percentiles.

Qualitative comparisons of measured data to USEPA Water Quality Standards (U.S. Environmental Protection Agency, 1999) were made when appropriate to assist in identification of potential water-quality problems. Water-quality data for the various constituents also may be compared to the latest USEPA ambient water-quality criteria for aquatic life maintained on the USEPA website (<http://www.epa.gov/OST/>) or Wisconsin water quality standards for surface waters (Wisconsin Administrative Code, Chapters NR102–105).

## Streambed Sediment and Biological Data

### Data Collection

Streambed-sediment data were collected once each year during low flow near Langlade and at Keshena on the Wolf River by use of methods described in Shelton and Capel (1994). Tissues of biota were collected concurrently. Sediment samples were composites of samples collected by hand with a Teflon scoop from each of 5 to 10 depositional zones (submerged during low streamflow) along a reach of approximately 150 m. Samples were collected from the upper 2 cm (most recent, oxidized layer) and the amount collected depended on the relative size of the depositional zone. Deposits of fine-grained sediment were sought out and sampled; thus, concentrations represent conditions in depositional areas of the streams, not the average concentrations for sediment throughout the stream reach. The composited samples from the reach were homogenized, and a bulk (<2 mm fraction) sample was removed for particle-size analysis. The rest of the composite sample was wet-sieved in the field, and the fine

(<0.062 mm) fraction was collected for trace-element analysis.

Methods for collection and processing of biota (Crawford and Luoma, 1994) included use of plastic implements (Teflon, polypropylene, or polyethylene) where appropriate for trace-element sampling. Quality-control procedures for the collection and processing of biota and sediment included collection of approximately 15 percent replicate samples and the use of clean techniques to minimize potential contamination.

Fish for tissue analyses were collected by the use of direct-current electrofishing gear. Depending on stream depth, stage, and other factors, either backpack-mounted or towed-barge electrofishing units were used. The target organism for capture was the white sucker (*Catostomus commersoni*). After capture, the fish were rinsed in native water, weighed, and measured for total length. Scale and spine samples were collected for age determination. Fish livers were removed, placed in pre-cleaned glass jars with teflon-lined lids, and frozen on dry ice and then shipped to the laboratory for analysis.

Caddisfly larvae (*Hydropsyche* spp. or *Ceratopsyche* spp.) were collected by handpicking from rocks and woody debris with plastic tweezers and PVC-gloved hands (figure 3). To minimize sediment in their guts, larvae were allowed to depurate for 4–6 hours in plastic bags containing native water. They were then placed in filtered deionized water (18 Mohm), counted into pre-cleaned glass jars with teflon-lined lids, frozen on dry ice, and shipped to the laboratory for analysis.

Benthic macroinvertebrates and algae in riffle habitat were sampled by use of methods established for the National Water Quality Assessment program (Porter and others, 1993; Cuffney and others, 1993). Riffle selection was based on the assumption that these areas represented the taxonomically richest habitat for the Wolf River. Cobble was the dominant substrate in both sampled stream reaches.

Benthic macroinvertebrate communities were sampled semi-quantitatively by use of a modified Surber sampler with 425- $\mu$ m mesh that was placed securely against the stream bottom, perpendicular to the current (figure 4). All cobble-sized rock in a 0.5-m by 0.5-m area of the stream bottom was scrubbed with a stiff brush. The stream bottom was then disturbed to a depth of approximately 10 cm with a rod and then by vigorous foot motion. During low flow in September 1998, six subsamples were collected from each reach, three in a downstream riffle area and three in an upstream riffle area. Subsamples were field elutriated with a bucket,

picked free of debris, and combined into one sample per reach. Samples were preserved with 70 percent nonde-natured ethanol and shipped to the laboratory for further processing.

Collections of benthic algal communities were made at the same time and in the same general location as the invertebrate-community sampling and consisted of quantitative samples. For each quantitative sample, algae were removed from a circular sampling area (approximately 2 cm in diameter) from five rocks in each of five locations from each site. An SG-92 sampling device, constructed of a syringe barrel and sealing O-ring, was used with a small brush to remove the algae. The 25 algal surface-area subsamples were then composited into a single quantitative algal sample of approximately 75 cm<sup>2</sup> for each site.

### Laboratory Analyses

Sediment and tissues were analyzed for trace elements at the USGS National Water Quality Laboratory in Denver, Colo. The sediment analyses included 46 major and trace elements (including two forms of carbon; inorganic and organic, as well as total carbon; appendixes 6 and 7). Biota were analyzed for a subset of 22 trace elements and for percent moisture (appendix 8). Concentrations of arsenic, cadmium, and selenium in biota were analyzed by ICP/MS; arsenic and selenium concentrations in sediment were analyzed by the use of hydride-generation AAS (atomic absorption spectrophotometry) and cadmium was analyzed by GFAA spectrometry. Trace-element analysis involved total digestions, and all concentrations in sediment and biota are given as micrograms per gram ( $\mu$ g/g) dry weight. Quality-control measures at the laboratory included comparisons to standard reference materials, spikes, and duplicates. Sediment particle size was analyzed at the USGS Sediment Laboratory in Iowa City, Iowa. Age determinations of fish based on scale and spine samples were done at the USGS Great Lakes Science Center in Ann Arbor, Mich.

The University of Wisconsin—Stevens Point, College of Natural Resources, Benthic Macroinvertebrate Laboratory (Dr. Stanley Szczytko), provided the species identification and enumeration and sample statistics for the macroinvertebrate samples. Samples were processed according to a rapid bioassessment protocol as described in Hilsenhoff (1987, 1988). Invertebrates were identified to the lowest practical level (generally species) by use of regional and global keys. At least 250



**Figure 3.** Method for collecting caddisfly larvae from woody debris and rocks for trace-element analysis.



**Figure 4.** Invertebrate community sampling method using a modified Surber net, Wolf River near Langlade biological site.

individuals were counted in each sample by use of a grid system.

Benthic algal samples were identified and enumerated by The Academy of Natural Sciences—Philadelphia, Patrick Center for Environmental Research, under the supervision of Dr. Frank Acker. The algal hierarchies follow those of Bold and Wynne (1985). Taxonomy and methods used were standard protocol used for USGS NAWQA benthic algal samples.

## Data Analyses

Invertebrate metrics computed included total taxa richness (species and genera) and percent Ephemeroptera-Plecoptera-Trichoptera (EPT). Percent EPT is the percentage of total EPT individuals to the total numbers of individuals in the sample. EPT taxa are considered to be pollution sensitive (Lenat, 1988). Indexes computed included Hilsenhoff Biotic Index (HBI) and Family Biotic Index (FBI), as described by Hilsenhoff (1987 and 1988), Shannon-Wiener diversity index (Brewer, 1979), and Mean Tolerance Value of all genera present (Lillie and Schlessler, 1994). Increasing HBI and FBI values indicate poorer water quality. The index of similarity (Odum, 1971) was computed to quantify the percentage of similar species at sites.

Analysis of the benthic algal data was threefold and included (1) basic summary descriptions of the algal taxa at sites, (2) comparison among sites, and (3) comparison to established indexes. Percent relative abundance of algal groups was computed for diatoms (division Bacillariophyta), green algae (division Chlorophyta), and euglenoids (division Euglenophyta). For nitrogen-fixers, Cuffney and others (1997), Bold and Wynne (1985), and Fairchild and Lowe (1984) were used for taxonomic reference.

The index of biological integrity for diatoms was computed according to Bahls (1993), using relative abundance data from richest-targeted-habitat samples. This index has three metrics: (1) Shannon-Wiener diversity index (Brewer, 1979), (2) pollution index, and (3) siltation index. The value for each index is given a score, and the lowest of all three scores is used to determine the biological integrity rating. The Shannon-Wiener diversity index for diatoms is computed in log base 2. The pollution index is based on the decimal fraction of diatoms in each of three tolerance groups (most tolerant, less tolerant, and sensitive) of Lange-Bertalot (1979) multiplied by the tolerance group rating. The pollution index therefore ranges from 1 (all most toler-

ant) to 3 (all sensitive). Our evaluation of diatom pollution index scores is based on Bahl's (1993) categories for Montana streams: <1.50 (severe pollution), 1.50 to 2.00 (moderate pollution), 2.01 to 2.50 (minor pollution), and >2.50 (no pollution). The siltation index is the sum of the percent relative abundance of silt-tolerant taxa (*Navicula*, *Nitzschia*, *Surirella*, and *Cylindrotheca*), and values range from 0 to 100. The resulting scores for diversity and siltation were calibrated with a method similar to that of Lenat (1993) using the 25th and 75th percentiles of data for 37 sites in the Western Lake Michigan Drainages sampled by the USGS NAWQA program during 1993–95 (B. Scudder, U.S. Geological Survey, Middleton, Wis., unpublished data). This calibration suggests that algal diversity values may indicate community stress as follows: <2.30 (high stress), 2.30 to 3.29 (moderate stress), 3.30 to 4.29 (minor stress), and >4.30 (no stress). Calibrated silt index ratings were: >80 (heavy siltation), 60–80 (moderate siltation), 40–60 (minor siltation), and <40 (no siltation). These rankings should be interpreted with caution due to the small sample size.

## CHARACTERISTICS OF STREAM WATER, SEDIMENT, AND BENTHIC COMMUNITIES

### Chemical Characteristics of Water

Water-quality samples were collected from stations on the Wolf River near Langlade, at Keshena, and at Shawano and analyzed for field-measured characteristics, major ions, nutrients, trace elements, and pesticides. Water discharge variability at Langlade and downstream at Shawano during 1986–98 are shown in figures 5 and 6. The basin area increases from about 463 mi<sup>2</sup> at Langlade to about 816 mi<sup>2</sup> at Shawano.

Although the Wolf River is not a major source of drinking water to the Reservation, comparison of Wolf River contaminant concentrations to the USEPA National Primary and Secondary Drinking Water Maximum Contaminant Levels (U.S. Environmental Protection Agency, 1999) is provided in several of the following discussions of water quality to assist in evaluations of the magnitude of river contamination. Readers who wish to understand water quality in greater detail than the discussion presented in this report are referred to the published USEPA (1999) drinking-water standards and ambient water-quality criteria. Also, "Study and Interpretation of the Chemical Characteris-

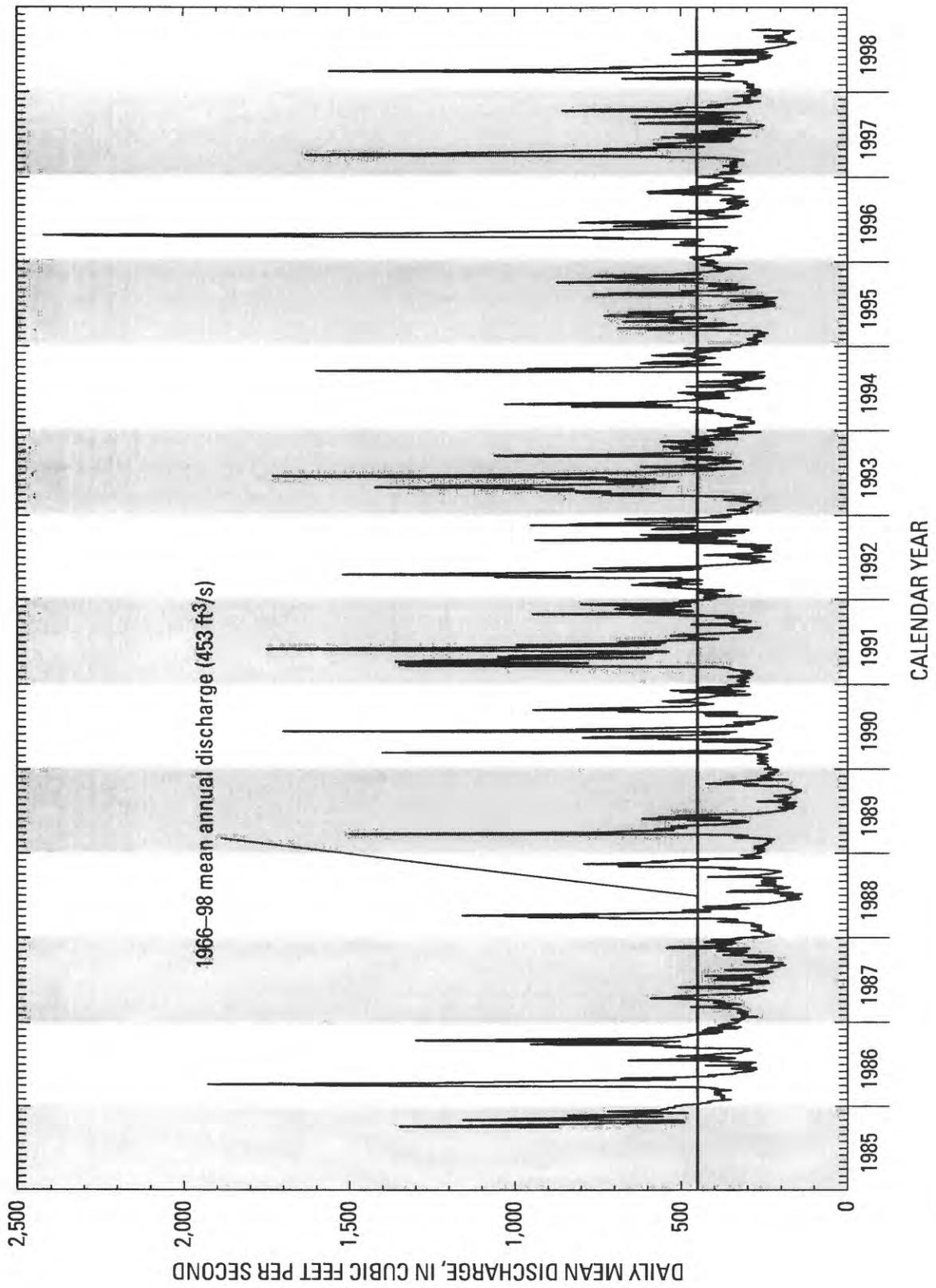


Figure 5. Daily mean discharge of the Wolf River at Langlade, station 04074950, 1985-98.

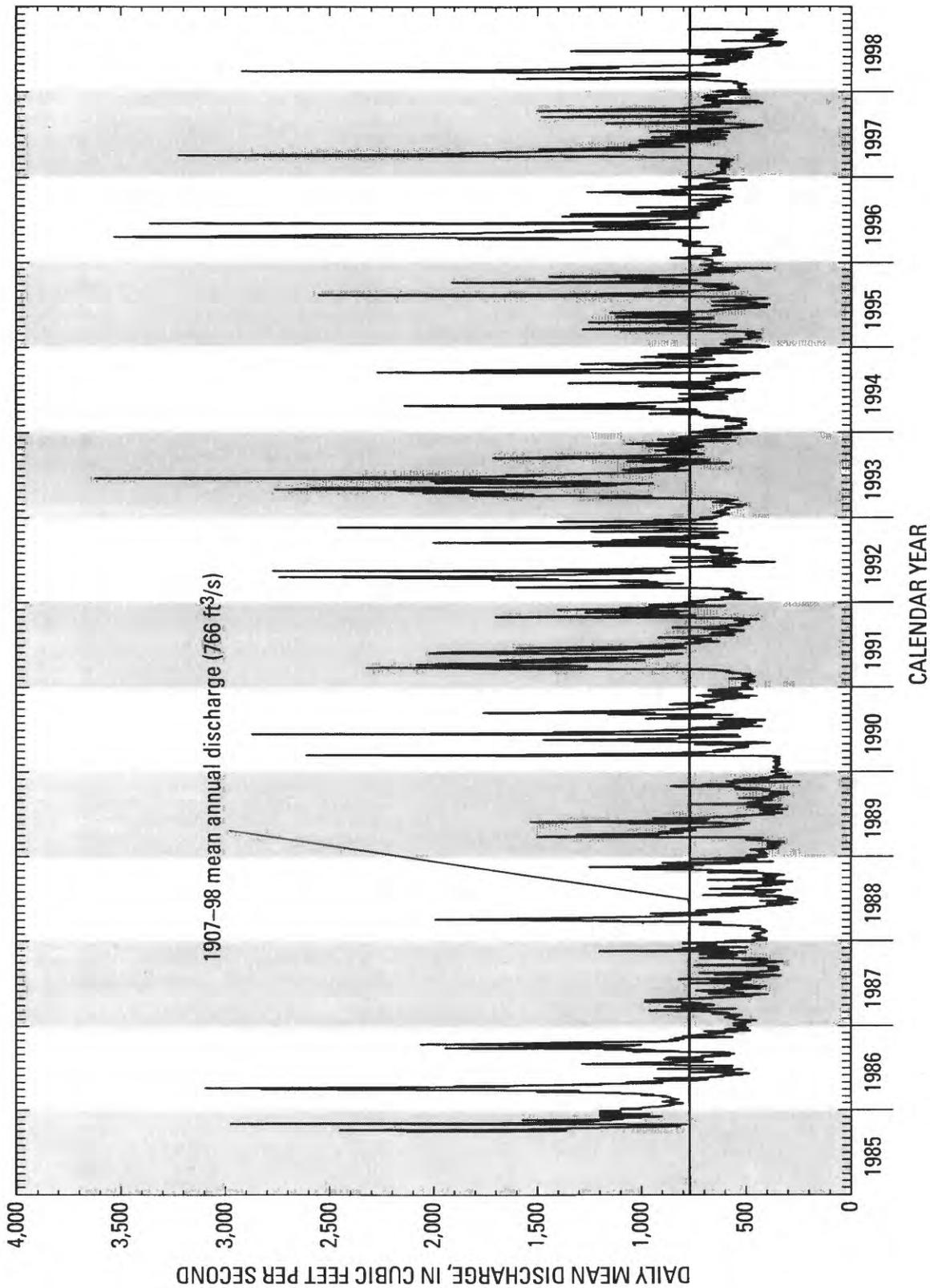


Figure 6. Daily mean discharge of the Wolf River at Shawano, station 04077400, 1985-98.

tics of Natural Water," by Hem (1992) provides additional information.

### Field Measurements

Multiparameter field instruments were used to measure pH, specific conductance, dissolved oxygen, and water temperature at the time of water-sample collection. The median pH of 104 samples measured at Langlade was 8.0 (table 4), and that of 28 samples measured at Keshena was 8.1 (table 5). These values are within the range of pH values from 6.5 to 8.5 reported by Hem (1992, p. 64) for river water in areas not affected by pollution. These values are not substantially different from the median pH of 7.6 for 47 samples collected at Shawano from 1989 through 1996 (table 6). Because rainfall is more acidic than surface or ground water that has been buffered by contact with more alkaline rocks and soil, changes in the pH of the Wolf River may fluctuate with the percentage of more acidic rain-runoff relative to the percentage of base flow that may be present in the river at any time.

Specific conductance, a measure of the ability of water to conduct electricity, is related to the concentration of dissolved ions (such as salts) in water. Mean specific conductance measured at Langlade (table 4) was 198  $\mu\text{S}/\text{cm}$ , and that downstream at Keshena was 226  $\mu\text{S}/\text{cm}$  (table 5). Mean specific conductance measured at Shawano during 1989 through 1996 was 233  $\mu\text{S}/\text{cm}$  (table 6). Substances contributing to specific conductance in the Wolf River on the Menominee Reservation primarily consist of ions derived from geological materials that come in contact with runoff and ground water.

Mean concentrations of dissolved oxygen in the Wolf River were near, at, or above saturation at all times in samples collected at Langlade, Keshena, and Shawano. Oxygen-saturated waters would be expected in a river such as the Wolf that has an adequate surface-area to volume ratio to provide interaction of water with oxygen in the atmosphere, and is relatively unaffected by wastes exerting a high biochemical oxygen demand (BOD) or chemical oxygen demand (COD) on the river.

Water temperatures measured upstream at Highway M near Langlade had a slightly lower mean and median than those measured at Keshena, which is a reflection of the channel conditions and shading by riparian vegetation.

### Major Ions

Water in the Wolf River on the Menominee Reservation is of a calcium-magnesium bicarbonate type (fig. 7). Concentrations of other commonly found major ions such as sodium, potassium, chloride, fluoride, and sulfate are present only at low concentrations (tables 4, 5, and 6). Total solids (residue) concentrations in the Wolf River were low at the three sampled sites, with mean concentrations ranging from 7 to 9 mg/L.

Water quality in the Wolf River is determined by water entering the Reservation from areas upstream, surface runoff on the Reservation, and also by ground water discharging to the river from the unconfined bedrock and overlying sand and gravel aquifers—this contributing ground water is also of a calcium-magnesium, bicarbonate type with low concentrations of dissolved solids, sulfate, and chloride (Krohelski and others, 1994, p. 10).

### Nutrients

Concentrations of nutrients, the various species of nitrogen and phosphorus, were low in samples collected at the three Wolf River sites (tables 4–6). Absence of excessive levels of nutrients indicates that the Wolf River is not substantially affected by sewage or septic-system discharges, runoff or ground water that is contaminated with agricultural fertilizer or animal manure wastes, nutrient-laden industrial discharges, or any other substantial sources.

#### Nitrogen

Water-quality analyses of nitrogen species in water for this project included "Kjeldahl" nitrogen, which is the sum of organic plus ammonia nitrogen concentrations, and separate analyses for ammonia and nitrite plus nitrate nitrogen. Total nitrogen is the sum of total Kjeldahl nitrogen plus nitrite and nitrate nitrogen. In general, in well-aerated water such as that in the Wolf River, organic nitrogen contributed by sewage, food or vegetation wastes, farm-animal wastes, or fertilizer runoff is converted first to ammonia, which is subsequently oxidized to nitrate. In oxygenated waters, nitrite is a short-lived, intermediate product that is formed during the oxidation of ammonium to nitrate, and virtually all of the nitrite plus nitrate values would actually be present as nitrate in the Wolf River.

**Table 4. Statistical summary of water-quality data, April 1986–September 1998, at the Wolf River at Highway M near Langlade, Wis., station 04075050**  
 [\* value estimated by using a log-probability regression to predict the values of data below the detection limit; <, less than; --, not calculated; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter]

Water-quality constituent	Sample size	Maximum	Minimum	Mean	Percentile				
					95	75	50 (Median)	25	5
Color, platinum cobalt scale	15	64	5	36	64	55	35	22	5
Specific conductance, µS/cm at 25°C	103	365	73	198	265	222	202	165	121
Water temperature, °C	105	25.5	0	11	24	19	11.1	1.2	0
Oxygen, dissolved, mg/L	60	15	8.2	11.0	14.7	12.5	11	9.2	8.2
Chemical oxygen demand, mg/L	16	31	<10.	*19	*31	*22	*17	*11	* <10.0
pH, field, standard unit	104	9.4	6.2	7.9	8.6	8.3	8	7.7	6.4
Residue, total, mg/L	24	17	<1.0	*6.7	*11	*8	*6	*4	* <1.0
Nitrogen, ammonia dissolved, mg/L as N	61	.13	<.01	*.04	*.08	*.05	*.0	*.02	* <.015
Nitrogen, ammonia, mg/L as N	36	.08	<.01	*.02	*.08	*.03	*.01	* <.010	* <.01
Nitrogen, nitrite, mg/L as N	28	.03	<.01	* <.01	*.03	* <.010	* <.010	* <.010	* <.01
Nitrogen, ammonia & organic, dissolved, mg/L as N	35	1	<.20	*.45	*.9	*.5	*.4	*.3	* <.20
Nitrogen, ammonia & organic, total, mg/L as N	27	.7	.2	.42	.7	.5	.4	.3	.2
NO <sub>2</sub> + NO <sub>3</sub> , dissolved, mg/L as N	63	.6	<.05	*.17	*.41	*.28	*.12	*.06	* <.05
Phosphorus, total, mg/L as P	61	.08	<.01	*.02	*.06	*.03	*.02	*.01	* <.01
Phosphorus, ortho, mg/L as P	54	.62	<.01	* <.01	*.02	*.01	* <.01	* <.01	* <.01
Carbon, organic dissolved, mg/L as C	21	10	3.2	6.6	10	8.25	6.3	5.0	3.2
Cyanide, total, mg/L as CN	50	<.01	<.01	<.01	--	--	--	--	--
Cyanide, dissolved, mg/L as CN	15	<.01	<.01	<.01	--	--	--	--	--
Hardness, total, mg/L as CaCO <sub>3</sub>	101	130	36	100.1	130	120	100	84.5	58.2
Calcium, dissolved, mg/L as Ca	101	30	8.2	22.3	29	26	23	19	13.1
Chloride, dissolved, mg/L as Cl	100	10	.4	2.8	4.2	3	2.6	2.4	2
Fluoride, dissolved, mg/L as F	97	.4	<.10	*.15	*.2	*.2	*.1	*.1	* <.10
Iron, total, µg/L as Fe	95	920	50	312	670	380	280	200	100
Iron, dissolved, µg/L as Fe	42	300	32	120	278	162.5	105	71	35
Magnesium, dissolved, mg/L as Mg	101	14	3.7	10.8	14	13	11	9.3	6.0
Manganese, total, µg/L as Mn	95	180	10	53.5	120	60	50	30	18
Manganese, dissolved, µg/L as Mn	42	19	4	9.6	15.7	11	10	7.3	5.0
Sodium, dissolved, mg/L as Na	101	3	.1	2.3	2.9	2.6	2.3	2.1	1.7
Potassium, dissolved, mg/L as K	101	6	.1	.94	1.3	1	.9	.7	.6
Sulfate, dissolved, mg/L as SO <sub>4</sub>	100	26	3.3	7.6	16.0	9.9	6.15	4.9	3.7
Silica, dissolved, mg/L as SiO <sub>2</sub>	97	14	3.5	8.4	13.1	10.5	7.9	6.25	4.1

**Table 5. Statistical summary of water-quality data, May 1995–September 1998, at the Wolf River at Keshena, Wis., station 04077100**

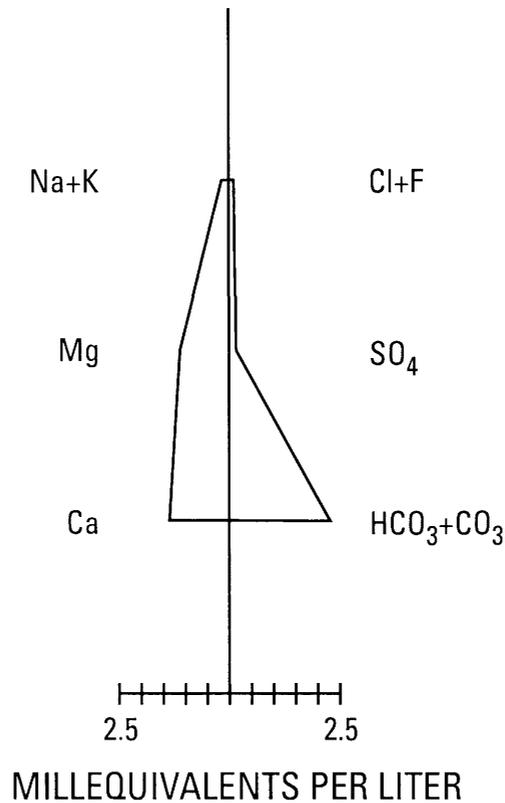
[\*, value estimated by using a log-probability regression to predict the values of data below the detection limit; --, not calculated; <, less than; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter]

Water-quality constituent	Sample size	Maximum	Minimum	Mean	Percentile				
					95	75	50 (Median)	25	5
Specific conductance, µS/cm at 25°C	28	305	102	226	301	258	236	198	112
Water temperature, °C	28	23.7	0.1	12.9	23.7	21	13.7	1.2	0.1
Oxygen, dissolved, mg/L	28	14.9	8.3	10.9	14.8	13.2	10.2	9.0	8.3
Chemical oxygen demand, mg/L	15	28	<10	*18	*28	*25	*17	*13	*10
pH, field, standard unit	28	8.6	6.8	8.0	8.6	8.275	8.1	7.9	6.8
Residue, total, mg/L	22	42	1	7	38	8	5	3.75	1.15
Nitrogen, ammonia, dissolved, mg/L as N	25	.06	<.015	*.02	*.05	*.03	*.02	*.02	*.02
Nitrogen, ammonia and organic, total, mg/L as N	25	.71	.23	.41	.71	.5	.4	.3	.2
NO <sub>2</sub> + NO <sub>3</sub> , dissolved, mg/L as N	25	.53	<.05	*.19	*.51	*.30	*.13	*.08	*.06
Phosphorus, total, mg/L as P	25	.06	<.01	*.02	*.06	*.02	*.02	*.01	*.01
Phosphorus, ortho, mg/L as P	25	.02	<.01	<.01	--	--	--	--	--
Carbon, organic dissolved, mg/L as C	20	11	3.1	6.3	10.9	8.4	5.6	4.0	3.1
Cyanide, total, mg/L as CN	15	.01	<.01	<.01	--	--	--	--	--
Cyanide, dissolved, mg/L as CN	15	<.01	<.01	<.01	--	--	--	--	--
Calcium, dissolved, mg/L as Ca	25	32	12	25.4	32	29	28	22.5	12.6
Chloride, dissolved, mg/L as CL	25	4.3	1.9	3.0	4.2	3.4	2.9	2.5	2.0
Fluoride, dissolved, mg/L as F	25	.27	.1	.18	.27	.2	.2	.15	.1
Iron, total, µg/L as Fe	24	860	100	292	777	347	260	202	102
Iron, dissolved, µg/L as Fe	25	300	37	110	297	135	87	62.5	37
Magnesium, dissolved, mg/L as Mg	25	17	5.4	12.4	17	14	14	10	5.8
Manganese, total, µg/L as Mn	24	160	30	55.8	152	67.5	42.5	30.2	30
Manganese, dissolved, µg/L as Mn	25	60	5	14.5	49.5	15.5	13	9.4	5.4
Sodium, dissolved, mg/L as Na	25	3	1.6	2.4	3.0	2.6	2.5	2.1	1.6
Potassium, dissolved, mg/L as K	25	1.3	.8	.93	1.2	1	.9	.84	.8
Sulfate, dissolved, mg/L as SO <sub>4</sub>	25	7.7	4.1	5.8	7.6	6.7	5.8	5	4.1
Silica, dissolved, mg/L as SiO <sub>2</sub>	25	13	4.9	8.4	12.7	11	7.9	6.4	5.1

**Table 6. Statistical summary of water-quality data, October 1989–September 1996, at the Wolf River near Shawano, Wis., station 04077400**

[\*, value estimated by using a log-probability regression to predict the values of data below the detection limit; --, not calculated; <, less than; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter]

Water-quality constituent	Sample size	Maximum	Minimum	Mean	Percentile				
					95	75	50 (Median)	25	5
Color, platinum cobalt scale	14	60	13	35	60	55	28	19.5	13
Specific conductance, µS/cm at 25°C	87	380	0	233	300	270	245	204	146
Water temperature, °C	87	32.5	0	10.6	24	19.6	10.7	1	0
Oxygen, dissolved, mg/L	38	14.7	5.7	10.4	14.6	12.5	9.6	8.3	6.5
pH, field, standard unit	47	8.4	6.4	7.6	8.3	8	7.6	7.3	6.54
Residue, total, mg/L	13	25	<1	8.9	*25.0	*10.5	*7.0	*5.0	*4.0
Nitrogen, ammonia, dissolved, mg/L as N	46	0.1	<0.1	*.04	*.08	*.05	*.04	*.03	*.02
Nitrogen, nitrite, mg/L as N	25	.03	<0.1	<.01	--	--	--	--	--
Nitrogen, ammonia and organic, dissolved, mg/L as N	32	.7	<.20	*.41	*.70	*.50	*.40	*.30	*.20
Nitrogen, ammonia and organic, total, mg/L as N	14	.8	.3	.46	.8	.52	.4	.3	.3
NO <sub>2</sub> + NO <sub>3</sub> , dissolved, mg/L as N	46	.62	.05	.25	.61	.44	.18	.12	.06
Phosphorus, total, mg/L as P	46	.1	<.01	*.03	*.06	*.03	*.02	*.02	*.01
Phosphorus, ortho, mg/L as P	39	.03	<.01	*<.01	--	--	--	--	--
Carbon, organic dissolved, mg/L as C	8	9.5	4.1	7	9.5	8.7	7.1	5.7	4.1
Cyanide, total, mg/L as CN	1	<.01	--	--	--	--	--	--	--
Calcium, dissolved, mg/L as Ca	47	36	12	26.4	35	30	28	23	18
Chloride, dissolved, mg/L as Cl	47	5.6	2.1	3.5	5.1	4.2	3.2	3	2.2
Fluoride, dissolved, mg/L as F	47	.5	.1	.18	.26	.2	.2	.1	.1
Iron, total, µg/L as Fe	46	2,400	80	382	1,070	425	280	197.5	134
Iron, dissolved, µg/L as Fe	28	290	35	122	285	150	105	70	38
Magnesium, dissolved, mg/L as Mg	47	17	5.4	12.7	16.6	15	13	11	8.3
Manganese, total, µg/L as Mn	46	170	10	53	133	70	50	30	10
Manganese, dissolved, µg/L as Mn	28	66	7	25.6	60	35.5	24	11.5	7
Sodium, dissolved, mg/L as Na	47	4.2	1.6	2.5	3.3	2.7	2.4	2.3	1.7
Potassium, dissolved, mg/L as K	47	9.4	.1	1.14	1.5	1.1	1	.9	.7
Sulfate, dissolved, mg/L as SO <sub>4</sub>	47	12	4.2	7.0	11.6	8.2	6.6	5.7	4.5
Silica, dissolved, mg/L as SiO <sub>2</sub>	47	14	4.5	9.0	13.6	11	8.5	6.8	5.1



**Figure 7.** Proportions of major ions at Wolf River at Keshena, Wis., station 04077100, March 11, 1998.

Mean total nitrogen concentrations near Langlade and at Keshena were 0.59 mg/L, and 0.60 mg/L, respectively. Concentrations of total Kjeldahl nitrogen at Langlade and Keshena were low: a mean concentration of 0.42 mg/L for 27 samples collected at Langlade and a mean concentration of 0.41 mg/L for 25 samples collected at Keshena (tables 4 and 5). Concentrations of ammonia and nitrite plus nitrate were slightly higher in samples collected at Shawano 1989 through 1996 than those at Langlade and Keshena 1995 through 1998; however, concentrations of these nitrogen species were still quite low and do not indicate the presence of water-quality problems as compared to a standard such as the USEPA National Drinking Water Maximum Contaminant Level (MCL) of 10 mg/L for nitrite plus nitrate nitrogen.

### Phosphorus

Two species of phosphorus were analyzed in the water samples: a "total phosphorus" analysis that is the sum of particulate and dissolved phosphorus, and an analysis of "orthophosphorus," which comprises only

dissolved phosphorus. Sources of phosphorus in water are virtually the same as those reported above for nitrogen, with a possible addition of phosphate-based detergents or cleaning compounds that may be used and subsequently disposed of in the basin.

As with nitrogen, concentrations of phosphorus in water samples from the Wolf River at the three sites were low, indicating an absence of pollution in the river. The mean total phosphorus concentration for 61 samples collected at Langlade was 0.02 mg/L, for 25 samples collected at Keshena was also 0.02 mg/L, and for 46 samples collected at Shawano the mean was 0.03 mg/L. Mean orthophosphorus concentrations at all sites were less than the analytical detection limit of 0.01 mg/L.

### Trace Elements

Analyses for trace elements in Wolf River water for this project included the most common elements found in the Earth's crustal materials. With the exception of elevated concentrations of iron, manganese, and aluminum, trace elements that are abundant in the geologic

materials of the Wolf River Basin are present at only low concentrations in river water. In general, trace elements increasingly dissolve in water under increasingly acidic conditions—any substantial increase in the acidity of the Wolf River could cause larger quantities of trace elements that are presently bound in the highly mineralized rocks and sediment of the basin to dissolve and become mobilized.

Despite the low concentrations of most trace elements in the Wolf River water, some trace elements that are present may bioaccumulate and could potentially have a negative effect on fish and other animals in the food chain. Bioaccumulation of trace elements in fish is discussed under the heading “Fish Tissues” in the “Characteristics of Benthic Communities” section of this report.

Concentrations of iron and manganese in the Wolf River (tables 4, 5, and 6) are elevated because of dissolution of iron- and manganese-bearing materials associated with the igneous granites, syenite, and monzonite of the Precambrian bedrock and of materials in the overlying glacial till in the basin. Krohelski and others (1994, p. 10) reported that water from about three-quarters of sampled wells on the Reservation had high concentrations of iron and manganese. The iron and manganese in ground water directly contribute to the elevated levels of iron and manganese in Wolf River baseflow. Mean concentration of total iron in 95 Langlade samples was 312 µg/L (table 4), in 24 Keshena samples was 292 µg/L (table 5), and in 46 Shawano samples was 382 µg/L (table 6). These concentrations are near or greater than the USEPA Secondary MCL for iron in public water supplies of 300 µg/L. Elevated iron concentrations in water supplies are undesirable for esthetic reasons (such as color) and also because such water can stain laundry or plumbing fixtures. Mean concentration of total manganese in 95 samples collected from Langlade was 53.5 µg/L (as Mn), the mean concentration of 24 samples collected at Keshena was 55.8 µg/L, and the mean concentration of 46 samples collected at Shawano was 53.0, indicating high concentrations when compared to the USEPA Secondary MCL for manganese in public water supplies of 50 µg/L.

Barium, chromium, boron, zinc and mercury were occasionally detected at very low concentrations in water samples collected at Langlade, Keshena, and Shawano (tables 7,8, and 9). Barium is a common trace element associated with igneous rocks such as those that form the bedrock under the Menominee Reservation. The most common form of barium is barite (BaSO<sub>4</sub>),

which has a low to moderate solubility in freshwater. Mean concentrations of dissolved barium were low at the Langlade and Keshena sites, and even the maximum concentration of 14 µg/L in a sample collected at Keshena was substantially below a median concentration of 45 µg/L of barium in larger rivers of the United States (cited by Hem, 1992). The USEPA MCL for barium for public water supplies is 2 mg/L, about 2 orders of magnitude greater than the barium concentrations measured in the Wolf River. The maximum dissolved chromium concentration measured in Wolf River samples was 0.8 µg/L (as Cr) in one sample from each of the Langlade and Keshena sites, in comparison with the USEPA MCL of 100 µg/L. Boron and zinc are present at all three sites but concentrations do not represent a water-supply or human-health concern (Hem, 1992). The USEPA Secondary MCL for zinc in public water supplies is 5 mg/L. A maximum concentration of mercury of 1 µg/L (as Hg) in each sample collected at Langlade and Shawano is half of the USEPA MCL of 2 µg/L for public water supplies. Low-level mercury sampling techniques and analyses, (at the nanogram per liter level) of 13 samples each at Langlade and Keshena during 1996–98, however, indicated a maximum of 7.4 ng/L (.0074 µg/L) total mercury near Langlade and 6.7 ng/L (.0067 µg/L) total mercury at Keshena.

Low concentrations of total copper, total lead, and total nickel were generally detected in water samples collected near Langlade and at Keshena and Shawano. These low concentrations generally did not approach any USEPA MCL's for drinking water (U.S. Environmental Protection Agency, 1999). For example, the USEPA Secondary MCL for copper in public water supplies is 1,000 µg/L, and the maximum total copper found was 23 µg/L in a sample collected at Shawano (table 9). A maximum concentration of 67 µg/L of total lead was observed, however, in a sample near Langlade. The USEPA MCL for lead in public water supplies is 15 µg/L.

The only other trace element with mean concentrations above the detection limit was aluminum. Although aluminum is the third most abundant element in the Earth's outer crust, it has a low solubility in most natural waters of near-neutral pH such as the Wolf River. Many of the aquifer and regolith materials on the Reservation are silicate igneous rocks and residual clays that contain aluminum. Most aluminum present in water samples from the Wolf River was in particulates (total aluminum) instead of being dissolved in the water. Mean total aluminum concentration of 17 samples collected near

**Table 7.** Summary of trace-element data in water, April 1986–September 1998, at the Wolf River at Highway M near Langlade, Wis., station 04075050  
[ $\mu\text{g/L}$ , micrograms per liter;  $\text{ng/L}$ , nanogram per liter]

Water-quality constituent	Sample size	Number of detections	Maximum	Minimum	Mean
Aluminum, dissolved, $\mu\text{g/L}$ as Al	17	15	34	<10.0	11.9
Aluminum, total, $\mu\text{g/L}$ as Al	17	17	210	20	62.9
Antimony, dissolved, $\mu\text{g/L}$ as Sb	5	0	<1	<1	<1
Arsenic, dissolved, $\mu\text{g/L}$ as As	15	4	1	<1	<1
Arsenic, total, $\mu\text{g/L}$ as As	68	22	10	<1	<1
Barium, dissolved, $\mu\text{g/L}$ as Ba	17	17	13	7.2	10.2
Barium, total, $\mu\text{g/L}$ as Ba	66	4	200	<100	<100
Boron, dissolved, $\mu\text{g/L}$ as B	15	10	24	<16	13.8
Boron, total, $\mu\text{g/L}$ as B	17	12	30	<10	15.3
Cadmium, dissolved, $\mu\text{g/L}$ as Cd	15	2	0.2	<0.1	<1.0
Cadmium, total, $\mu\text{g/L}$ as Cd	68	4	4	<1	<1
Chromium, dissolved, $\mu\text{g/L}$ as Cr	15	4	.8	<.5	<.5
Chromium, hexavalent, $\mu\text{g/L}$ as Cr	5	0	<1	<1	<1
Chromium, total, $\mu\text{g/L}$ as Cr	69	31	22	<1	<1
Cobalt, dissolved, $\mu\text{g/L}$ as Co	15	3	.6	<.5	<1
Cobalt, total, $\mu\text{g/L}$ as Co	17	0	<1	<1	<1
Copper, dissolved, $\mu\text{g/L}$ as Cu	15	1	2.5	<.5	<.5
Copper, total, $\mu\text{g/L}$ as Cu	70	57	9	<1	2.9
Lead, dissolved, $\mu\text{g/L}$ as Pb	15	1	.6	<.5	<.5
Lead, total, $\mu\text{g/L}$ as Pb	68	40	67	<5, <1	7
Lithium, dissolved, $\mu\text{g/L}$ as Li	17	0	<10	<4	<4
Lithium, total, $\mu\text{g/L}$ as Li	17	1	20	<10	<10
Mercury, total recoverable, $\mu\text{g/L}$ as Hg	56	6	1	<.1	<.1
Mercury, dissolved, $\text{ng/L}$ as Hg <sup>1</sup>	13	13	4.6	.5	1.7
Mercury, total recoverable, $\text{ng/L}$ as Hg <sup>1</sup>	13	13	7.4	.8	2.8
Molybdenum, dissolved, $\mu\text{g/L}$ as Mo	5	0	<1	<1	<1
Nickel, dissolved, $\mu\text{g/L}$ as Ni	15	1	1	<1	<1
Nickel, total, $\mu\text{g/L}$ as Ni	67	35	6	<50, <1	1.8
Selenium, dissolved, $\mu\text{g/L}$ as Se	15	0	<1	<1	<1
Selenium, total, $\mu\text{g/L}$ as Se	41	0	<1	<1	<1
Silver, dissolved, $\mu\text{g/L}$ as Ag	17	0	<1	<.2	<1
Silver, total, $\mu\text{g/L}$ as Ag	67	6	9	<1	<1
Thallium, dissolved, $\mu\text{g/L}$ as Tl	17	0	<.5	<.5	<.5
Thallium, total, $\mu\text{g/L}$ as Tl	12	0	<1	<1	<1
Uranium, natural, $\mu\text{g/L}$ as U	17	2	1	<1	<1
Zinc, dissolved, $\mu\text{g/L}$ as Zn	15	12	5.5	<.5	1.8
Zinc, total, $\mu\text{g/L}$ as Zn	67	20	120	<10	<10

<sup>1</sup>1996–98

**Table 8. Summary of trace-element data in water, May 1995–September 1998, at the Wolf River at Keshena, Wis., station 04077100**

[ $\mu\text{g/L}$ , micrograms per liter;  $\text{ng/L}$ , nanograms per liter]

Water-quality constituent	Sample size	Number of detections	Maximum	Minimum	Mean
Aluminum, dissolved, $\mu\text{g/L}$ as Al	15	11	26	4.6	10.6
Aluminum, total, $\mu\text{g/L}$ as Al	15	15	200	20	66.7
Antimony, dissolved, $\mu\text{g/L}$ as Sb	5	0	<1	<1	<1
Arsenic, dissolved, $\mu\text{g/L}$ as As	15	3	1	<1	<1
Arsenic, total, $\mu\text{g/L}$ as As	13	2	1	<1	<1
Barium, dissolved, $\mu\text{g/L}$ as Ba	15	15	14	7.9	11.2
Barium, total, $\mu\text{g/L}$ as Ba	12	0	<100	<100	<100
Beryllium, dissolved, $\mu\text{g/L}$ as Be	5	0	<1	<1	<1
Boron, dissolved, $\mu\text{g/L}$ as B	15	11	19	9.3	13.4
Boron, total, $\mu\text{g/L}$ as B	15	13	20	<10	14.7
Cadmium, dissolved, $\mu\text{g/L}$ as Cd	15	1	.3	<.1	<1
Cadmium, total, $\mu\text{g/L}$ as Cd	13	0	<1	<1	<1
Chromium, dissolved, $\mu\text{g/L}$ as Cr	15	6	.8	<.5	.56
Chromium, hexavalent, $\mu\text{g/L}$ as Cr	5	0	<1	<1	<1
Chromium, total, $\mu\text{g/L}$ as Cr	13	2	2	<1	<1
Cobalt, dissolved, $\mu\text{g/L}$ as Co	15	1	.6	<.5	<.5
Cobalt, total, $\mu\text{g/L}$ as Co	15	0	<1	<1	<1
Copper, dissolved, $\mu\text{g/L}$ as Cu	15	2	2.8	<.5	<.5
Copper, total, $\mu\text{g/L}$ as Cu	15	3	1	<1	<1
Lead, dissolved, $\mu\text{g/L}$ as Pb	15	1	2.4	<.5	<.5
Lead, total, $\mu\text{g/L}$ as Pb	13	2	2	<1	<1
Lithium, dissolved, $\mu\text{g/L}$ as Li	15	0	<4	<4	<4
Lithium, total, $\mu\text{g/L}$ as Li	15	0	<10	<10	<10
Mercury, dissolved, $\text{ng/L}$ as $\text{Hg}^1$	13	13	3.4	.5	1.7
Mercury, total recoverable, $\text{ng/L}$ as $\text{Hg}^1$	13	13	6.7	.8	2.8
Molybdenum, dissolved, $\mu\text{g/L}$ as Mo	5	0	<1	<1	<1
Nickel, dissolved, $\mu\text{g/L}$ as Ni	15	0	<1	<1	<1
Nickel, total, $\mu\text{g/L}$ as Ni	15	0	<50	<1	<50
Selenium, dissolved, $\mu\text{g/L}$ as Se	15	0	<1	<1	<1
Selenium, total, $\mu\text{g/L}$ as Se	4	0	<1	<1	<1
Silver, dissolved, $\mu\text{g/L}$ as Ag	15	0	<1	<.2	<.2
Silver, total, $\mu\text{g/L}$ as Ag	15	0	<1	<1	<1
Thallium, dissolved, $\mu\text{g/L}$ as Tl	15	0	<.5	<.5	<.5
Thallium, total, $\mu\text{g/L}$ as Tl	12	0	<1	<1	<1
Uranium, natural, dissolved	15	9	1.6	<1	<1
Zinc, dissolved, $\mu\text{g/L}$ as Zn	15	11	7.9	<.5	1.8
Zinc, total, $\mu\text{g/L}$ as Zn	15	0	<10	<10	<10

<sup>1</sup>1996–98

**Table 9.** Summary of trace-element data in water, October 1989–September 1996, at the Wolf River near Shawano, Wis., station 04077400  
[ $\mu\text{g/L}$ , micrograms per liter]

Water-quality constituent	Sample size	Number of detections	Maximum	Minimum	Mean
Arsenic, total, $\mu\text{g/L}$ as As	17	4	2	<1	<1
Barium, total, $\mu\text{g/L}$ as Ba	18	2	100	<100	<100
Cadmium, total, $\mu\text{g/L}$ as Cd	18	2	3	<1	<1
Chromium, total, $\mu\text{g/L}$ as Cr	18	7	3	<1	<1
Copper, total, $\mu\text{g/L}$ as Cu	18	17	23	<1	4.1
Lead, total, $\mu\text{g/L}$ as Pb	18	16	5	<1	1.6
Nickel, total, $\mu\text{g/L}$ as Ni	18	13	40	<1	4.2
Mercury, total recoverable, $\mu\text{g/L}$ as Hg	18	1	1	<.1	<.1
Silver, total, $\mu\text{g/L}$ as Ag	18	0	<1	<1	<1
Zinc, total, $\mu\text{g/L}$ as Zn	18	6	100	<10	<10

Langlade was  $62.9 \mu\text{g/L}$ , with a maximum measured value of  $210 \mu\text{g/L}$  (table 7). Similar total aluminum concentrations were found in 15 samples collected at Keshena (table 8). The USEPA Secondary Maximum Contaminant Level for aluminum in water delivered from a public water supply is 50 to  $200 \mu\text{g/L}$ . A comparison of aluminum concentrations in water samples collected from the Wolf River with the USEPA standard indicates that the River contains elevated levels of aluminum relative to most natural waters—probably because of the natural erosion and weathering of the aluminum-rich basin materials.

## Pesticides

Screening-level analysis was done for 61 pesticides and pesticide metabolites in water samples collected near Langlade and at Keshena from 1995 to 1998 (tables 10 and 11). Atrazine and alachlor are widely used for season-long weed control in corn, sorghum, and other crops. Trace amounts of atrazine (maximum concentration of  $0.031 \mu\text{g/L}$  at Langlade) and a degradation product deethylatrazine (maximum  $0.032 \mu\text{g/L}$  at Langlade) were detected in samples collected at Langlade and Keshena during May through September of each year. Alachlor and metolachlor were also detected one time at Langlade. Lindane and metolachlor were detected once at Keshena. The USEPA MCL for atrazine in public water supplies is  $3 \mu\text{g/L}$ , and that for alachlor is  $2 \mu\text{g/L}$ .

Likely sources of atrazine and alachlor to the Wolf River include leaching of herbicides that may be applied to cropped land upstream from the sampling sites and atmospheric deposition to the basin. No other pesticides were present at concentrations above the analytical detection limits. Very low concentrations or nondetections of pesticides are expected in areas such as the Upper Wolf River Basin that are not intensively farmed.

## Physical and Chemical Characteristics of Sediment

### Particle Size

The percentages of the bulk sediment samples (<2 mm) from the Wolf River near Langlade for 1995–98 that were silt/clay (< $0.062 \text{ mm}$ ) averaged 67.2 percent and ranged from 36.2 to 100 percent; the clay fractions (< $0.004 \text{ mm}$ ) averaged 34.2 percent and ranged from 16.0 to 50.5 percent (table 12). For the Keshena site, particle size analyses indicated that an average of 28.2 percent of the bulk sediment was silt and clay. This is the fraction that was collected for trace element analysis at both sites. Clay made up a smaller part of the depositional sediment, averaging 12.5 percent. The percentage of clay making up the sample was fairly consistent among years. The silt and clay fraction in depositional sediment from the Wolf River near Langlade was more variable among years than that from

**Table 10.** Summary of pesticide data (dissolved), 1995–98, for the Wolf River at Highway M near Langlade, Wis., station 04075050

[µg/L, micrograms per liter; <, less than; --, not computed]

Compound name	Sample size	Number of detects	Maximum	Minimum	Mean
2,6-Diethylaniline	4	0	<0.003	<0.003	
Acetochlor, µg/L	8	0	<.050	<.002	--
Alachlor, µg/L	8	1	.002	<.002	--
Ametryn, µg/L	4	0	<.050	<.050	--
Atrazine, µg/L	8	6	.031	<.050	0.015
Atrazine, deethyl-, µg/L	8	5	.032	<.050	.008
Atrazine, deisopropyl-, µg/L	4	0	<.050	<.050	--
Azinphos, methyl-, µg/L	4	0	<.001	<.001	--
Benfluralin, µg/L	4	0	<.002	<.002	--
Bromacil, µg/L	4	0	<.050	<.050	--
Butachlor, µg/L	4	0	<.050	<.050	--
Butylate, µg/L	8	0	<.050	<.002	--
Carbaryl (Sevin), µg/L	4	0	<.003	<.003	--
Carbofuran, µg/L	4	0	<.003	<.003	--
Carboxin, µg/L	4	0	<.050	<.050	--
Chlorpyrifos, µg/L	4	0	<.004	<.004	--
Cyanazine, µg/L	8	0	<.200	<.004	--
Cycloate, µg/L	4	0	<.050	<.050	--
DCPA (Dacthal), µg/L	4	0	<.002	<.002	--
DDE, µg/L	4	0	<.006	<.006	--
Diazinon, µg/L	4	0	<.002	<.002	--
Dieldrin, µg/L	4	0	<.001	<.001	--
Diphenamid, µg/L	4	0	<.050	<.050	--
Disulfoton, µg/L	4	0	<.017	<.017	--
EPTC (Eptam), µg/L	4	0	<.002	<.002	--
Ethalfuralin, µg/L	4	0	<.004	<.004	--
Ethoprophos, µg/L	4	0	<.003	<.003	--
Fonofos, µg/L	4	0	<.003	<.003	--
HCH, alpha-, µg/L	4	0	<.002	<.002	--
Hexazinone, µg/L	4	0	<.050	<.050	--
Lindane, µg/L	4	0	<.004	<.004	--
Linuron, µg/L	4	0	<.002	<.002	--

**Table 10.** Summary of pesticide data (dissolved), 1995–98, for the Wolf River at Highway M near Langlade, Wis., station 04075050—Continued

[ $\mu\text{g/L}$ , micrograms per liter; <, less than; --, not computed]

Compound name	Sample size	Number of detects	Maximum	Minimum	Mean
Malathion, $\mu\text{g/L}$	4	0	<.005	<.005	--
Metolachlor, $\mu\text{g/L}$	8	1	.004	<.002	--
Metribuzin, $\mu\text{g/L}$	8	0	<.070	<.004	--
Molinate, $\mu\text{g/L}$	4	0	<.004	<.004	--
Napropamide, $\mu\text{g/L}$	4	0	<.003	<.003	--
Parathion, ethyl-, $\mu\text{g/L}$	4	0	<.004	<.004	--
Parathion, methyl-, $\mu\text{g/L}$	4	0	<.006	<.006	--
Pebulate, $\mu\text{g/L}$	4	0	<.004	<.004	--
Pendimethalin, $\mu\text{g/L}$	4	0	<.004	<.004	--
Permethrin, cis, $\mu\text{g/L}$	4	0	<.005	<.005	--
Phorate, $\mu\text{g/L}$	4	0	<.002	<.002	--
Pronamide, $\mu\text{g/L}$	4	0	<.003	<.003	--
Prometon, $\mu\text{g/L}$	8	0	<.050	<.018	--
Prometryn, $\mu\text{g/L}$	4	0	<.050	<.050	--
Propachlor, $\mu\text{g/L}$	8	0	<.050	<.007	--
Propanil, $\mu\text{g/L}$	4	0	<.004	<.004	--
Propazine, $\mu\text{g/L}$	4	0	<.050	<.050	--
Propargite I and II, $\mu\text{g/L}$	4	0	<.013	<.013	--
Simazine, $\mu\text{g/L}$	8	0	<.050	<.005	--
Simetryn, $\mu\text{g/L}$	4	0	<.050	<.050	--
Thiobencarb, $\mu\text{g/L}$	4	0	<.002	<.002	--
Tebuthiuron, $\mu\text{g/L}$	4	0	<.010	<.010	--
Terbufos, $\mu\text{g/L}$	4	0	<.013	<.013	--
Triallate, $\mu\text{g/L}$	4	0	<.001	<.001	--
Trifluralin, $\mu\text{g/L}$	8	0	<.050	<.002	--
Terbacil, $\mu\text{g/L}$	8	0	<.050	<.007	--
Vernolate, $\mu\text{g/L}$	4	0	<.050	<.050	--

**Table 11.** Summary of pesticide data (dissolved), 1995–98, for the Wolf River at Keshena, Wis., station 04077100

[µg/L, micrograms per liter; <, less than; --, not computed]

Compound name	Sample size	Number of detects	Maximum	Minimum	Mean
2,6-Diethylaniline, µg/L	3	0	<0.003	<0.003	--
Acetochlor, µg/L	7	0	<.05	<.002	--
Alachlor, µg/L	7	0	<.05	<.002	--
Ametryn, µg/L	4	0	<.05	<.05	--
Atrazine, µg/L	7	5	.03	.007	0.017
Atrazine, deethyl-, µg/L	7	4	.034	.003	--
Atrazine, deisopropyl-, µg/L	4	0	<.05	<.05	--
Azinphos, methyl-, µg/L	3	0	<.001	<.001	--
Benfluralin, µg/L	3	0	<.002	<.002	--
Bromacil, µg/L	4	0	<.05	<.05	--
Butachlor, µg/L	4	0	<.05	<.05	--
Butylate, µg/L	7	0	<.05	<.002	--
Carbaryl (Sevin), µg/L	3	0	<.003	<.003	--
Carbofuran, µg/L	3	0	<.003	<.003	--
Carboxin, µg/L	4	0	<.05	<.05	--
Chlorpyrifos, µg/L	3	0	<.004	<.004	--
Cyanazine, µg/L	7	0	<.20	<.004	--
Cycloate, µg/L	4	0	<.05	<.05	--
DCPA (Dacthal), µg/L	3	0	<.002	<.002	--
DDE, µg/L	3	0	<.006	<.006	--
Diazinon, µg/L	3	0	<.002	<.002	--
Dieldrin, µg/L	3	0	<.001	<.001	--
Disulfoton, µg/L	3	0	<.017	<.017	--
EPTC (Eptam), µg/L	3	0	<.002	<.002	--
Ethalfuralin, µg/L	3	0	<.004	<.004	--
Ethoprophos, µg/L	3	0	<.003	<.003	--
Fonofos, µg/L	3	0	<.003	<.003	--
HCH, alpha-, µg/L	3	0	<.002	<.002	--
Hexazinone, µg/L	4	0	<.05	<.05	--
Lindane, µg/L	3	1	.008	<.004	--
Linuron, µg/L	3	0	<.002	<.002	--
Malathion, µg/L	3	0	<.005	<.005	--

**Table 11.** Summary of pesticide data (dissolved), 1995–98, for the Wolf River at Keshena, Wis., station 04077100—Continued

[ $\mu\text{g/L}$ , micrograms per liter; <, less than; --, not computed]

Compound name	Sample size	Number of detects	Maximum	Minimum	Mean
Metolachlor, $\mu\text{g/L}$	7	1	<.05	<.002	--
Metribuzin, $\mu\text{g/L}$	7	0	<.05	<.004	--
Molinate, $\mu\text{g/L}$	3	0	<.004	<.004	--
Napropamide, $\mu\text{g/L}$	3	0	<.003	<.003	--
Parathion, ethyl-, $\mu\text{g/L}$	3	0	<.004	<.004	--
Parathion, methyl-, $\mu\text{g/L}$	3	0	<.006	<.006	--
Pebulate, $\mu\text{g/L}$	3	0	<.004	<.004	--
Pendimethalin, $\mu\text{g/L}$	3	0	<.004	<.004	--
Permethrin, <i>cis</i> , $\mu\text{g/L}$	3	0	<.005	<.005	--
Phorate, $\mu\text{g/L}$	3	0	<.002	<.002	--
Pronamide, $\mu\text{g/L}$	3	0	<.003	<.003	--
Prometon, $\mu\text{g/L}$	7	0	<.05	<.018	--
Prometryn, $\mu\text{g/L}$	4	0	<.05	<.05	--
Propachlor, $\mu\text{g/L}$	7	0	<.05	<.007	--
Propanil, $\mu\text{g/L}$	3	0	<.004	<.004	--
Propargite I and II, $\mu\text{g/L}$	3	0	<.013	<.013	--
Propazine, $\mu\text{g/L}$	4	0	<.05	<.05	--
Simetryn, $\mu\text{g/L}$	4	0	<.05	<.05	--
Simazine, $\mu\text{g/L}$	7	0	<.05	<.005	--
Thiobencarb, $\mu\text{g/L}$	3	0	<.002	<.002	--
Tebuthiuron, $\mu\text{g/L}$	3	0	<.010	<.010	--
Terbufos, $\mu\text{g/L}$	3	0	<.013	<.013	--
Triallate, $\mu\text{g/L}$	3	0	<.001	<.001	--
Trifluralin, $\mu\text{g/L}$	7	0	<.05	<.002	--
Terbacil, $\mu\text{g/L}$	7	0	<.05	<.007	--
Vernolate, $\mu\text{g/L}$	4	0	<.05	<.05	--

**Table 12.** Particle-size data for bulk (<2 mm) depositional sediment collected from the Wolf River near Langlade and at Keshena, 1995–98 [mm, millimeter]

Site and year	Sediment fraction	
	Percent silt/clay (<0.062 mm)	Percent clay (<0.004 mm)
Wolf River near Langlade		
1995	83.2	45.1
1996	49.5	25.4
1997	36.2	16.0
1998	100	50.5
Mean value	67.2	34.2
Wolf River at Keshena		
1996	23.3	9.4
1997	28.7	12.9
1998	32.5	15.3
Mean value	28.2	12.5

Keshena. An effort was made to sample the same or similar locations at this site among years, and these results indicate more variability in sediment size for certain depositional areas within this reach of the river.

### Trace Elements

Concentrations of most trace elements were low in fine streambed sediment from the Wolf River sites at Keshena and near Langlade (table 13; appendix 6 and 7). Concentrations observed were within the ranges found by Scudder and others (1997) for the Western Lake Michigan Drainages and were generally on the lower ends of these ranges. Concentrations of chromium, copper, nickel, and zinc were similar to or less than the 25th percentile reported for other NAWQA study areas across the Nation by Rice (1999; also see Peters and others, 1998). Arsenic and selenium concentrations found at the Keshena and Langlade sites were higher than those reported for fine sediment from some sites in the Western Lake Michigan Drainages (Scudder and others, 1997), and they were above the 75th percentile for NAWQA study units (Rice, 1999). The concentrations were still relatively low, however, when compared to other sites with similar land use and bedrock type in the Western Lake Michigan Drainages and likely represent contributions from natural sources. Scudder and others (1997) found that forested land use and igneous/metamorphic bedrock were related to

higher arsenic and selenium concentrations in streambed sediment. Sediment arsenic concentrations, if converted to bulk sediment concentrations using data in table 12, still would not exceed the Canadian Sediment Quality Guidelines (Canadian Council of Ministers of the Environment, 1999) or the Threshold Effects Concentration calculated by McDonald and others (2000). Lead concentrations for the two Wolf River sites would be below these guidelines and were below the 50th percentile of values reported by Rice (1999). These concentrations also were near the median for forested-land-use sites and far below ranges found at urban and large mixed-land-use rivers sampled by Scudder and others (1997).

Concentrations of most elements at the downstream Keshena site did not show any significant increase when compared to the upstream site near Langlade. Exceptions were for lanthanum, lead, neodymium, and manganese concentrations, which were higher at the downstream Keshena site.

No temporal trends were apparent in the data collected to date. Data available are insufficient for statistical examination of trends. The data do provide a useful baseline to which future measurements may be compared.

**Table 13.** Statistical summary of trace elements and carbon in fine (<0.062 mm) streambed sediment from the Wolf River near Langlade and at Keshena, Wis., 1995–98

[Trace-element concentrations are shown in micrograms per gram, and carbon concentrations are shown in percent. All concentrations are for dry weight. The number of samples, N, was 4 at Langlade and 3 at Keshena; \*, one value less than the minimum reporting level was included in computation of the average and standard deviation by substituting a value equal to one-half the minimum detection limit; --, not computed]

Element	Langlade			Keshena		
	Mean	Standard deviation	Maximum	Mean	Standard deviation	Maximum
Antimony	0.3	0.1	0.4	0.3	0.1	0.4
Arsenic	9.5	2.3	12	13	3.5	17
Barium	342	43.5	380	347	5.8	350
Beryllium	<1	--	<1	<1	--	<1
Bismuth	<10	--	<10	<10	--	<10
Cadmium	.7	.1	.7	.7	.1	.7
Cerium	41	8.4	51	53	5.7	58
Chromium	51	7.0	57	53	7.2	59
Cobalt	6.6	1.2	8.0	6.8	1.3	8.0
Copper	15	2.8	19	15	2.6	18
Europium	<2	--	<2	<2	--	<2
Gallium	*6.2	*3.3	10	*5.6	*3.5	9.0
Gold	<8	--	<8	<8	--	<8
Holmium	<4	--	<4	<4	--	<4
Lanthanum	23	5.9	30	30	2.6	32
Lead	20	2.1	22	24	1.7	26
Lithium	10	1.0	12	11	1.5	13
Manganese	2,200	540	2,900	3,200	380	3,500
Mercury	.1	0	.1	.1	0	.1
Molybdenum	<2	--	<2	<2	--	<2
Neodymium	19.8	4.5	25.0	24.3	2.5	27.0
Nickel	11	1.1	12	11	1.2	12
Niobium	6.3	2.0	8.0	*5.0	*3.0	8.0
Scandium	5.7	1.0	7.0	5.6	.7	6.0
Selenium	1.8	.1	1.9	1.7	.1	1.8
Silver	.3	.3	.7	.3	.1	.4
Strontium	77	11	87	77	5.9	81
Sulfur	.3	0	.4	.3	0	.4
Tantalum	<40	--	<40	<40	--	<40
Thorium	8.2	4.0	11	8.4	3.2	11
Tin	<5	--	<5	<5	--	<5
Titanium	.2	0	.2	.2	0	.2
Uranium	4.0	.9	4.7	3.0	.6	3.6
Vanadium	53	7.9	60	51	7.4	57
Ytterbium	1.8	.4	2.0	1.9	.2	2.0
Yttrium	18	3.5	22	21	2.3	22
Zinc	87	9.0	99	85	3.8	89
Carbon, organic	13.5	.7	14.3	12.8	1.0	13.5
Carbon, inorganic	.2	.1	.3	.3	0	.3
Carbon, Total	13.7	.7	14.5	13.1	1.0	13.8

**Table 14.** Statistical summary of trace elements in white sucker (*Catostomus commersoni*) livers from the Wolf River near Langlade and at Keshena, Wis., 1995–98

[Trace-element concentrations are shown in micrograms per gram dry weight. The number of composite samples, N, was 4 at Langlade and 3 at Keshena; \*, one value less than the minimum reporting level was included in computation of the average and standard deviation by substituting a value equal to one-half the minimum detection limit; --, not computed]

Element	Langlade			Keshena		
	Mean	Standard deviation	Maximum	Mean	Standard deviation	Maximum
Water (percent)	80.4	2.6	83.4	81.5	0.7	81.9
Antimony	<.3	--	<.5	<.4	--	<.4
Arsenic	*.32	.06	.40	*.36	.15	.48
Barium	*1.28	2.02	4.77	1.48	1.96	3.72
Beryllium	<.3	--	<.5	<.4	--	<.4
Boron	.88	.49	1.6	.63	.15	.80
Cadmium	<.3	--	<.5	<.4	--	<.4
Chromium	.69	.08	.80	.76	.21	1.00
Cobalt	<.3	--	<.5	<.4	--	<.4
Copper	18.7	9.46	28.3	44.7	24.2	59.3
Lead	<.3	--	<.5	<.4	--	<.4
Manganese	6.43	1.26	7.97	19.6	11.2	31.4
Mercury	<.10	--	<.10	*.15	.22	.4
Molybdenum	*.54	.19	.70	.79	.25	.96
Nickel	<.3	--	<.5	<.4	--	<.4
Selenium	3.3	.48	3.7	4.3	.81	5.2
Silver	<.3	--	.40	*.38	.16	.50
Strontium	<2.00	--	8.14	3.20	5.08	9.06
Uranium	<.3	--	<.5	<.4	--	<.4
Vanadium	<.24	--	.41	*.44	.23	.64
Zinc	76.3	12.2	88.9	111	35.3	145

## Characteristics of Benthic Communities

Results of sampling for benthic community characteristics and trace element concentrations in biota at the Langlade and Keshena sites on the Wolf River indicate that the algal and invertebrate communities are in very good to excellent condition and most trace elements in biota are at low or undetectable concentrations.

## Trace Elements

### Fish Tissues

Fish collected from the Langlade and Keshena sites on the Wolf River appeared generally healthy with regard to external morphology. No external anomalies were observed in white sucker collected from either site in 1995 through 1998, with the exception of one fish found with anchor worms at the Langlade site in 1997.

Most of the fish collected for trace-element analysis were 1–3 years old. In 1995, all fish from the Langlade site were 1 year old, and in 1996 through 1998 most or all fish collected from this site were 1–3 years old. The range and median ages of fish collected from the Keshena site were similar for the 1996 through 1997 collections. Fish collected were generally 2–3 years old, with a median age of 3 years. In 1998, the median age of fish from the Keshena site was 4 years for the regular sample and 3 years for the quality-control sample.

Analyses results revealed low concentrations of most trace elements in white sucker livers from the Langlade and Keshena sites (table 14; appendix 8). Total concentrations of arsenic and silver in white sucker livers from both sites were at or near analytical detection limits, and concentrations of antimony, beryllium, cadmium, cobalt, lead, nickel, and uranium were all below detection limits. The maximum tissue manganese concentration at the Keshena site was almost four

times higher than at the Langlade site, possibly reflecting the higher sediment manganese concentrations at the Keshena site. Concentrations of most other trace elements were similar to the lowest concentrations found by Fitzpatrick and others (1995) and Scudder and others (1997) for livers of white sucker collected from the Upper Illinois River Basin and Western Lake Michigan Drainages, respectively.

The exceptions to the otherwise low trace-element concentrations found in white sucker livers were for chromium, copper, mercury, and selenium. When converted to wet weight, all chromium concentrations found at the Langlade and Keshena sites were above the 85th percentile elevated-data level for livers from all freshwater fish collected in California's Toxic Substances Monitoring Program (Rasmussen, 1997); however, the elevated-data level lumps all freshwater species collected in that program and may not be directly comparable. The maximum concentration of 1.0  $\mu\text{g/g}$  chromium found at the Keshena site is low compared to concentrations found in white sucker livers collected by Fitzpatrick and others (1995) and Scudder and others (1997). Concentrations of other trace elements were below elevated-data levels reported for freshwater fish collected in the Toxic Substances Monitoring program.

Copper concentrations were higher at the Keshena site in 1997 and 1998 compared with concentrations found in 1996 and all dates from the Langlade site. These concentrations from the Keshena site were higher than some concentrations found by Fitzpatrick and others (1995) and Scudder and others (1997), including a background concentration of 6.6  $\mu\text{g/g}$  copper found in white sucker livers from the Upper Peninsula of Michigan by Scudder and others (1997). Copper concentrations found in white sucker livers from the Wolf River sites are not high compared to concentrations at urban sites sampled by Fitzpatrick and others (1995). Although sediment copper concentrations were similar and low at the Langlade and Keshena sites during 1995–1998, the fish from Keshena may be accumulating copper from another nearby source not measured that contains more biologically available copper. Copper is associated with urban runoff (such as from domestic sewage and land fills), agricultural chemicals, and industrial sources. Fish movement from the Keshena site would be limited to a few miles by Keshena Falls upstream and the dam downstream with 2 small western tributaries in between.

An elevated concentration of 0.4  $\mu\text{g/g}$  mercury was found in white sucker livers from the Keshena site in 1998, although all other concentrations in samples of white sucker livers from the Keshena and Langlade sites were near or below the detection limits (detection limits ranged from 0.10 to 0.01  $\mu\text{g/g}$  mercury) and sediment concentrations were low (0.08 to 0.10  $\mu\text{g/g}$  mercury). In addition, the associated quality control sample contained only 0.17  $\mu\text{g/g}$  mercury. As noted above, the median age of fish in the regular sample was 4 years, whereas the median age was 3 for the quality control sample; older organisms would be expected to accumulate higher concentrations of certain trace elements such as mercury so this may be why there was more mercury in the regular sample. In addition, the fact that this one value was an anomaly compared with other samples from this site indicates that one or more fish collected in the composite sample may have migrated from another area where the higher mercury concentration was accumulated such as wetland-drained areas where higher concentrations of biologically available methyl mercury could occur (Hurley and others, 1995). Atmospheric deposition is the major source of mercury to aquatic environments (Krabbenhoft and Rickert, 1995). This concentration is higher than that found for white sucker livers at some other sites in the Midwest by Fitzpatrick and others (1995), Scudder and others (1997), and Brigham and others (1998).

The average selenium concentration in white sucker livers was higher at the Keshena site (4.3  $\mu\text{g/g}$  Se) than at the Langlade site. This concentration also was high compared to a concentration at approximately background concentration (2.9  $\mu\text{g/g}$ ) in white sucker livers reported by Scudder and others (1997) but within the midrange of values found by Fitzpatrick and others (1995). The selenium concentrations in fish from the Wolf River may be associated with naturally occurring sources, such as the igneous metamorphic bedrock in the region. Scudder and others (1997) found that higher selenium concentrations in fine streambed sediment were correlated with sandy/sand and gravel surficial deposits, such as those found in the Wolf River drainage, as well as forested land use.

Agreement between trace-element concentrations in the regular sample and the quality-control sample of fish livers was close for the 1997 and 1998 data set, with the exception of the mercury concentrations discussed above. No quality-control samples were collected for fish in 1995 or 1996.

**Table 15.** Statistical summary of trace elements in whole caddisfly larvae (*Hydropsyche/Ceratopsyche* spp.) from the Wolf River near Langlade and at Keshena, Wis., 1995–98

[Trace-element concentrations are shown in micrograms per gram dry weight. The number of composite samples, N, was 4 at Langlade and 3 at Keshena; \*, one value less than the minimum reporting level was included in computation of the average and standard deviation by substituting a value equal to one-half the minimum detection limit; --, not computed]

Element	Langlade			Keshena		
	Mean	Standard deviation	Maximum	Mean	Standard deviation	Maximum
Water (%)	82.3	2.09	84.1	84.8	0.67	85.6
Arsenic	1.64	0.26	2.03	1.45	.23	1.65
Barium	34.8	14.3	50.6	59.2	12.9	67.8
Boron	3.2	.85	4.6	3.0	1.0	3.9
Beryllium	<.3	--	<.3	<.5	--	<.8
Cadmium	<.3	--	<.3	<.5	--	<.8
Cobalt	.42	.07	.50	.34	.06	.39
Chromium	2.1	.27	2.4	2.2	.30	2.5
Copper	11.1	1.38	13.4	11.4	1.62	13.0
Mercury	<.1	--	<.1	<.04	--	.04
Manganese	1,110	501	1,890	1,000	214	1,240
Molybdenum	1.6	.22	1.8	1.6	.25	1.9
Nickel	.52	.11	.6	.46	.08	.52
Lead	.79	.19	.98	.84	.12	.94
Antimony	<.3	--	<.3	<.5	--	<.8
Selenium	.76	.32	1.2	.91	.16	1.0
Silver	<.3	--	<.3	<.5	--	<.78
Strontium	1.3	.25	1.6	1.3	.17	1.4
Uranium	<.3	--	.31	<.5	--	<.8
Vanadium	2.1	.38	2.5	1.9	.49	2.4
Zinc	108	17.4	135	126	15.7	142

### Caddisfly Tissues

With the exception of silver, beryllium, cadmium, antimony, and uranium, the remaining trace elements examined were detected in all seven samples of caddisfly larvae from the Langlade and Keshena sites (table 15; appendix 8). Mercury was detected in three samples, but concentrations were low and near the minimum detection limit. For other trace elements, concentrations in caddisfly larvae were low compared to those at other sites sampled by Scudder and others (1997), and these reflect the low trace-element concentrations in water and streambed sediment described elsewhere in this report. Although arsenic concentrations in streambed sediment appeared somewhat elevated, likely reflecting the igneous-metamorphic bedrock of the drainage, concentrations were not high ( $\leq 2 \mu\text{g/g}$  dry weight) in caddisfly larvae from the Wolf River sites compared with other USGS sites sampled in the West-

ern Lake Michigan Drainages (Scudder and others, 1997). Scudder and others (1997) found a correlation between total concentrations of arsenic in streambed sediment and caddisfly larvae. In that study, caddisfly larvae from forested sites had significantly higher concentrations of arsenic; however, interpretations may have been influenced by the fact that most forested sites were underlain by igneous-metamorphic bedrock. Cain and others (1992) analyzed cadmium, copper, lead, and zinc in composite samples of the same genus of caddisfly larvae from reference sites minimally affected by human activity in Montana, and concentrations for these trace elements were similar to those found in caddisfly larvae in project samples from the Wolf River.

Concentrations of trace elements in caddisfly larvae were similar at the Keshena and Langlade sites. Although concentrations of manganese increased from

**Table 16.** Benthic macroinvertebrate metrics with respect to relative abundance in richest-targeted habitat for the Wolf River at Keshena and near Langlade, Wis., 1998

[EPT, Ephemeroptera-Plecoptera-Trichoptera genera; FBI, Family Biotic Index; HBI, Hilsenhoff Biotic Index using species level identification; total score possible for HBI, FBI, and Mean Tolerance Value is 10]

Benthic macroinvertebrate metric	Metric value	
	Langlade	Keshena
Number of species	48	48
Number of genera	44	41
Total number of individuals in sample	258	387
Number of Ephemeroptera genera	9	9
Number of Plecoptera genera	2	2
Number of Trichoptera genera	12	10
Percent EPT genera	52.3	51.2
FBI <sup>1</sup>	2.76	3.58
HBI <sup>2</sup>	2.70	3.19
Shannon-Wiener Diversity	4.05	4.41
Mean Tolerance Value <sup>3</sup>	3.15	3.31

<sup>1</sup>FBI: 0.00–3.75 Excellent, organic pollution unlikely.

<sup>2</sup>HBI: 0.00–3.50 Excellent, no apparent organic pollution.

<sup>3</sup>Mean Tolerance Value categories are same as for the HBI.

1995 to 1998 at both sites, data are insufficient to determine whether this is a statistically significant trend.

### Invertebrate Communities

A total of 48 species of macroinvertebrates were identified at each site (total taxa richness), with similar numbers of genera represented at both sites (appendix 9). Relative abundance of invertebrates was greater at Keshena. Of the EPT taxa, the order Trichoptera was the most abundant at these sites. The order Plecoptera was represented by only 2 genera, and Ephemeroptera and Trichoptera were represented by 9–12 genera. The taxa richness of EPT genera was slightly less at Keshena. The relatively large percentages (>50 percent) for EPT at Langlade and Keshena (table 16) indicate good water quality at these sites (Lenat, 1988) when compared to percent EPT values reported by Rheume and others (1996) and Lenz and Rheume (2000) for tributaries in the Western Lake Michigan drainages with similar environmental setting but some agricultural land use. The index of similarity was 0.71 (71 percent) for the Langlade and Keshena sites. Out of 48 total species at each site, 34 species

were present at both, and this suggests the two sites are fairly similar in their community composition.

The family (FBI) and species (HBI) level biotic indexes also indicated very good to excellent water quality and suggested slightly better water quality at the Langlade site compared to the downstream site at Keshena. The computed indexes were smaller at the Langlade site. The HBI values at Keshena and at Langlade site indicated excellent water quality with no apparent organic (organic matter or nutrient) enrichment (values between 0.00 and 3.50 as defined in Hilsenhoff, 1987). The FBI at Langlade was well within the range (0.00 to 3.75) for excellent water quality as defined by Hilsenhoff (1988). The FBI for the regular sample at Keshena was near the upper end of the range, and the value for the replicate was in the range (3.76–4.25) that indicated very good water quality but possible slight organic pollution. Mean tolerance values were similar at Keshena and Langlade and indicated excellent water quality; a slightly larger value at the Keshena site indicates that there are more pollution-tolerant species at this site. Shannon-Wiener diversity was relatively high at both sites, and a slightly higher diversity at a downstream river site is to be expected. The replicate value for diver-

**Table 17.** Distribution of benthic algal taxa with regard to phylum for the Wolf River near Langlade, and at Keshena, Wis., 1998

Phylum	Percent relative abundance		Percent biovolume	
	Langlade	Keshena	Langlade	Keshena
<i>Chlorophyta</i> (green algae)	2.8	3.0	1.4	7.0
<i>Bacillariophyta</i> (diatoms)	19	22	96	91
<i>Cyanophyta</i> (blue-green algae)	78	75	1.8	2.0
<i>Rhodophyta</i> (red algae)	.30	0	.47	0

sity at Keshena was 4.14, indicating little difference in diversity between the two sites. Mean tolerance values and EPT percentages indicated better water-quality at Langlade and Keshena than at a site on the Popple River in Wisconsin; FBI values at Keshena were similar to those at the Popple River (Lenz and Rheume, 2000). The Popple River drains the same bedrock and surficial deposit types but wet instead of dry forest is the dominant land use and cover.

In April 1991, Szczytko (1991) sampled the Wolf River 40 yards downstream of the Highway 47 bridge in approximately the same reach as our study. He used methods described by Hilsenhoff (1987, 1988). Any comparisons between the two studies must consider potential differences due to methods and timing of sampling, even though the same laboratory analyzed Szczytko's 1991 and our 1998 data sets. Szczytko found an average of 41 species (range 34 to 59) and 33 genera (range 27 to 48) in his two sets of five replicate samples from this site. These values are similar to what we found in 1998. The percent EPT was 40.9 in his study compared to 51.2 in our study. Although not directly comparable, the 4.41 Shannon-Wiener diversity index from our study and his mean of 4.42 for Margalef's diversity index both indicate a diverse assemblage of benthic macroinvertebrates at the Keshena site. Szczytko also found a mean HBI value of 4.16, within the "very good" water quality classification, and an FBI of 4.40, indicating "good" water quality. These HBI and FBI values from 1991 are higher than those we found in 1998. This suggests that water-quality conditions have improved during this time period.

### Algal Communities

For species richness, a total of 58 algal taxa were identified from the Wolf River at Keshena, including 48 diatom taxa representing 83 percent of all algal taxa (appendix 10). Although 22 percent of the algal relative

abundance in cells per square centimeter (cells/cm<sup>2</sup>) was due to diatoms, diatoms contributed 91 percent of the total algal biomass (table 17). In contrast, the percent relative abundance of blue-green algae was 75 percent, making up only 2.0 percent of the total algal biomass of the sample. Green algae made up 3.0 percent of the algal relative abundance and 7.0 percent of the biomass. *Audouinella violacea*, a freshwater red alga, was found in low (0.66 percent) relative abundance in the quality-control replicate sample from this site but was not found in the regular sample. This taxon may have been missed in the regular sample as a consequence of its small numbers and laboratory subsampling during processing. Freshwater red algae are common only in relatively pristine waters (Sheath and Hambrook, 1990). Nitrogen-fixing algae, including certain types of both diatoms and blue-green algae, made up 8.5 percent of the relative abundance of all algae. Nitrogen-fixing benthic algae are indicative of low nitrogen concentrations in the water column and although they are favored by nutrient-poor conditions, they may be found in abundance with high phosphorus enrichment (Burkholder, 1996; Cuffney and other, 1997). Nitrogen and phosphorus concentrations were low in our water samples from both sites.

At the Wolf River near Langlade site, 52 algal taxa were identified. A similar percentage (81 percent) of diatom taxa were found at this site compared to the Keshena site, and diatoms made up most (96 percent) of the algal biomass. Although blue-green algal cells were relatively abundant (78 percent) in the sample, their biomass (<2.0 percent) was insignificant compared to that of diatoms. The freshwater red alga *Audouinella violacea* also was found in low (0.30 percent) relative abundance at this site. Compared to the Keshena site, nitrogen-fixing algae were much more abundant at Langlade, making up 28 percent of the relative abundance of all algae.

**Table 18.** Benthic algal metrics for diatoms with respect to relative abundance in richest-targeted habitat for the Wolf River near Langlade and at Keshena, Wis., 1998

[Silt and pollution indexes were determined according to Bahls (1993) and calibrated for Western Lake Michigan tributaries to assign the biological index value. Shannon-Wiener diversity index values are in log base 2]

Benthic algal metric	Langlade	Keshena
Percent pollution tolerant	4.2	7.2
Percent pollution sensitive	78	76
Shannon Wiener Diversity Index <sup>1</sup>	3.65	4.38
Silt Index <sup>2</sup>	7.8	11
Pollution Index <sup>3</sup>	2.63	2.54
Biological index <sup>4</sup>	4 (Excellent)	4 (Excellent)

<sup>1</sup>Diversity Index: <2.30 (high stress), 2.30–3.29 (moderate stress), 3.30–4.29 (minor stress), >4.30 (no stress).

<sup>2</sup>Silt Index: >80 (heavy siltation), 60–80 (moderate siltation), 40–60 (minor siltation), <40 (no siltation).

<sup>3</sup>Pollution Index: <1.50 (severe pollution), 1.50–2.00 (moderate pollution), 2.01–2.50 (minor pollution), >2.50 (no pollution).

<sup>4</sup>Biological Index: 1 (poor), 2 (fair), 3 (good), 4 (excellent).

Shannon-Wiener diversity values for diatoms differed between the two sites (table 18). A high diversity value of 4.38 indicates no stress on the community at Keshena. Lower diatom diversity was found upstream at Langlade, but the value of 3.65 still indicates high diversity and minor or no stress on the community. This increase in diversity downstream may be a result of greater productivity that occurs as a river increases in size. The silt index, or percentage of diatoms that are considered to be silt tolerant, was low at 11 percent relative abundance at Keshena and slightly lower at Langlade, at 7.8 percent. This finding indicates that siltation is not a problem at either site for diatoms. Most of the diatoms at both sites are those considered to be pollution intolerant (76 percent of the diatom relative abundance at Keshena; 78 percent at Langlade). Tolerant diatoms made up only 7 percent and 4 percent, respectively, of the diatom relative abundance at the two sites. Pollution indexes for both streams were greater than 2.50 and indicate no pollution at these sites. The overall biological integrity of these two sites, based on diversity, siltation, and pollution indexes for diatoms, is excellent.

## SUMMARY AND CONCLUSIONS

Water quality of the Wolf River is largely unaffected by human activities along the entire reach on the

Menominee Indian Reservation as represented by water samples collected near Langlade and at Keshena. In general, no significant differences in water-quality were found in data collected upstream from the Wolf River near Langlade and downstream at Keshena and Shawano during water years 1986 through 1998. Water samples were analyzed for major ions, nutrients, trace elements, and pesticides. Bottom sediments were analyzed for trace elements and particle size. Biological organisms were collected and characterized to provide index values used to determine water and habitat quality.

High concentrations of calcium, magnesium, and iron were measured, all of which contribute to natural water hardness in the study area. Levels of Kjeldahl (ammonia plus organic) nitrogen detected at Langlade and Keshena were low: a mean concentration of 0.45 mg/L was measured at Langlade, and a mean concentration of 0.41 mg/L was measured at Keshena. Concentrations of phosphorus in water samples from the Wolf River at the three sites also were low. The mean concentration of 61 total phosphorus samples collected at Langlade was 0.02 mg/L; the mean concentration of 25 total phosphorus samples collected at Keshena was 0.02 mg/L; and 46 samples collected at Shawano had a mean concentration of 0.03 mg/L. Mean concentrations for orthophosphorus were below the analytical detection limit (0.01 mg/L) at the three sites.

A wide variety of trace elements are present in the Wolf River that originate from geologic materials and natural weathering in the basin. Most concentrations generally do not approach USEPA water-quality standards for public water supplies, however, the water had elevated levels of iron and manganese. Trace amounts of atrazine (maximum concentration of 0.031 µg/L at Langlade), deethylatrazine (maximum 0.032 µg/L at Langlade), and alachlor (maximum of 0.002 µg/L) were detected in samples collected at Langlade and Keshena during May through September of each year.

Low concentrations of most trace elements were found in streambed sediment at the Langlade and Keshena sites on the Wolf River. Arsenic and selenium concentrations at the sampled sites were high compared to other sites in the Western Lake Michigan Drainages and other NAWQA study units in the Nation; however, these concentrations may be related to the forested land use or igneous-metamorphic bedrock of the drainage. For the Wolf River at Keshena site, particle size analyses for water years 1996–98 showed that an average of 28.2 percent of the bulk (<2 mm) sediment was <0.062 mm (silt and clay), and this is the fraction that was collected for trace element analysis. Clay (<0.004 mm) made up a smaller part of the depositional sediment, averaging 12.5 percent.

Tissues of fish and aquatic invertebrates collected once each year from 1995 through 1998 at the Langlade and Keshena sites were low in concentrations of most trace elements. Arsenic and silver in fish livers from both sites were at or near analytical detection limits, and concentrations of antimony, beryllium, cadmium, cobalt, lead, nickel, and uranium were all below detection limits. Concentrations of most other trace elements in fish were low, as based on comparisons to literature values. The exceptions were for chromium, copper, mercury, and selenium; however, these concentrations are not at levels of concern. Concentrations of all trace elements analyzed in whole caddisfly larvae also were low compared to those reported in the literature.

For the invertebrate and algal community data collected in 1998, a total of 48 species of macroinvertebrates were identified at each site, with similar numbers of genera represented at both: 41 at Keshena and 44 at Langlade. Relative abundance of invertebrates was greater at Keshena. Of the EPT taxa, the order Trichoptera was the most abundant at these sites. The order Plecoptera was represented by only two genera, and Ephemeroptera and Trichoptera were represented by 9–12 genera. The taxa richness of EPT genera was

slightly less at Keshena. The percentage EPT was 52 at Keshena and 77 at Langlade, and these relatively large percentages suggest very good to excellent water quality at these sites. A total of 52 algal taxa identified at the Wolf River near Langlade site. Diatoms made up 96 percent of the algal biomass. A total of 58 algal taxa were identified from the Wolf River at Keshena, including 48 diatom taxa (83 percent). Although diatoms accounted for just 22 percent of the algal relative abundance, in cells per square centimeter, diatoms contributed 91 percent of the total algal biomass. Most of the diatoms at both sites are considered to be pollution intolerant, and the overall biological integrity of the sites, based on diatom metrics, is excellent.

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# **APPENDIXES 1–10**

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**Appendix 1.** Constituents and minimum reporting levels for the U.S. Geological Survey National Water-Quality Laboratory for major ions, chemical oxygen demand, residue, and specific conductance in water samples during 1986–98

[ $\mu\text{S}/\text{cm}$ , microsiemens per centimeter;  $\text{mg}/\text{L}$ , milligrams per liter;  $\mu\text{g}/\text{L}$ , micrograms per liter]

Constituent	Minimum reporting level
Calcium	0.020 mg/L
Chloride	.29 mg/L
Fluoride	.10 mg/L
Iron	10 $\mu\text{g}/\text{L}$
Magnesium	.014 mg/L
Manganese	2.2 $\mu\text{g}/\text{L}$
Potassium	.24 mg/L
Silica	.09 mg/L
Sodium	.09 mg/L
Sulfate	.31 mg/L
Chemical oxygen demand	10 mg/L
Residue, suspended, 105 degrees Celsius	1 mg/L
Specific conductance, laboratory	2.6 $\mu\text{S}/\text{cm}$

**Appendix 2.** Constituents and minimum reporting levels for the U.S. Geological Survey National Water-Quality Laboratory for nutrients in water samples during 1986–98

[ $\text{mg}/\text{L}$ , milligrams per liter]

Constituent	Minimum reporting level
Ammonia nitrogen (dissolved)	0.02 mg/L
Ammonia plus organic nitrogen, total	.10 mg/L
Nitrite plus nitrate (dissolved)	.1, .05 mg/L
Orthophosphate (dissolved)	.01 mg/L
Phosphorus, total	.01 mg/L

**Appendix 3.** Constituents and minimum reporting levels for the U.S. Geological Survey National Water-Quality Laboratory for trace elements in water samples during 1986–98 [mg/L, milligrams per liter; µg/L, micrograms per liter; ng/L, nanograms per liter]

Constituent	Minimum reporting level
Aluminum, total	10 µg/L
Aluminum, dissolved	10, 5 µg/L
Antimony, total	1.0 µg/L
Arsenic, total	1 µg/L
Arsenic, dissolved	1.0 µg/L
Barium, total	100 µg/L
Barium, dissolved	2.0 µg/L
Beryllium, total	2 µg/L
Boron, total	10 µg/L
Boron (dissolved)	16 and 4 µg/L
Cadmium, total	1.0 µg/L
Cadmium, dissolved	1.0 and 0.1 µg/L
Chromium, total	1.0 µg/L
Chromium, dissolved	.5 µg/L
Cobalt, total	1.0 µg/L
Cobalt, dissolved	.5 µg/L
Copper, total	1.0 µg/L
Copper, dissolved	1.0 and 0.5 µg/L
Cyanide, total	.010 mg/L
Cyanide, dissolved	.010 mg/L
Lead, total	5. µg/L
Lead, dissolved	1.0 and 0.5 µg/L
Lithium, total	10 µg/L
Lithium, dissolved	4 µg/L
Mercury, total	.1 µg/L
Mercury, total by USGS Wisconsin District Laboratory	.1 ng/L
Nickel, total	50 and 1.0 µg/L
Nickel, dissolved	1.0 µg/L
Selenium, total	1.0 µg/L
Selenium, dissolved	1.0 µg/L
Silver, total	1.0 µg/L
Silver, dissolved	1.0 and 0.2 µg/L
Thallium, total	1.0 µg/L
Thallium (dissolved)	.5 µg/L
Uranium, dissolved	1.0 µg/L
Zinc, total	10 µg/L
Zinc, dissolved	1.0 and 0.5 µg/L

**Appendix 4.** Constituents and minimum reporting levels for the U.S. Geological Survey National Water-Quality Laboratory for pesticides analyzed from 1995–96  
[µg/L, micrograms per liter]

<b>NWQL Schedule 2001</b>	
<b>Compound name</b>	<b>Minimum reporting level</b>
Acetochlor	0.002 µg/L
Alachlor	.002 µg/L
Atrazine	.001 µg/L
Atrazine, deethyl-	.002 µg/L
Azinphos, methyl-	.001 µg/L
Benfluralin	.002 µg/L
Butylate	.002 µg/L
Carbaryl (Sevin)	.003 µg/L
Carbofuran	.003 µg/L
Chlorpyrifos	.004 µg/L
Cyanazine	.004 µg/L
DCPA (Dacthal)	.002 µg/L
DDE	.006 µg/L
Diazinon	.002 µg/L
Dieldrin	.001 µg/L
EPTC (Eptam)	.002 µg/L
Ethalfuralin	.004 µg/L
Ethoprophos	.003 µg/L
Fonofos	.003 µg/L
HCH, alpha-	.002 µg/L
Lindane	.004 µg/L
Linuron	.002 µg/L
Malathion	.005 µg/L
Metolachlor	.002 µg/L
Metribuzin	.004 µg/L
Molinate	.004 µg/L
Napropamide	.003 µg/L
Parathion, ethyl-	.004 µg/L
Parathion, methyl-	.006 µg/L
Pebulate	.004 µg/L
Pendimethalin	.004 µg/L
Permethrin, cis	.005 µg/L
Phorate	.002 µg/L
Pronamide	.003 µg/L
Prometon	.018 µg/L
Propachlor	.007 µg/L
Propanil	.004 µg/L
Propargite I and II	.013 µg/L
Simazine	.005 µg/L
Thiobencarb	.002 µg/L
Tebuthiuron	.010 µg/L
Terbufos	.013 µg/L
Triallate	.001 µg/L
Trifluralin	.002 µg/L
Terbacil	.007 µg/L

**Appendix 5.** Constituents and minimum reporting levels for the U.S. Geological Survey National Water-Quality Laboratory for pesticides analyzed in water samples during 1997 and 1998  
[µg/L, micrograms per liter]

<b>NWQL Schedule 1379</b>	
<b>Constituent</b>	<b>Minimum reporting level</b>
Acetochlor	0.050 µg/L
Alachlor	.050 µg/L
Ametryn	.050 µg/L
Atrazine	.050 µg/L
Atrazine, deethyl	.050 µg/L
Atrazine, deisopropyl	.050 µg/L
Bromacil	.05 µg/L
Butachlor	.05 µg/L
Butylate	.05 µg/L
Carboxin	.05 µg/L
Cyanazine	.200 µg/L
Cycloate	.05 µg/L
Diphenamid	.05 µg/L
Hexazinone	.05 µg/L
Metolachlor	.050 µg/L
Metribuzin	.050 µg/L
Prometon	.050 µg/L
Prometryn	.050 µg/L
Propachlor	.05 µg/L
Propazine	.050 µg/L
Simazine	.050 µg/L
Simetryn	.05 µg/L
Terbacil	.05 µg/L
Trifluralin	.05 µg/L
Vernolate	.05 µg/L

**Appendix 6.** Concentrations of trace elements in fine streambed sediment (less than 0.062 mm) from sites on the Wolf River in the vicinity of the Menominee Indian Reservation

Date	Element concentration (micrograms per gram dry weight)																		
	Arsenic	Barium	Beryllium	Boron	Cadmium	Cerium	Chromium	Cobalt	Copper	Europium	Gallium	Gold	Holmium	Lanthanum	Lead	Lithium	Mercury	Manganese	Molybdenum
<b>Wolf River at Highway M near Langlade, Wis., station 4075050</b>																			
10/26/95	6.5	380	<1	<10	0.7	39	7	49	13	<2	7	<8	<4	18	22	10	0.1	2,100	<2
9/23/96	12	380	<1	<10	.7	51	8	57	19	<2	10	<8	<4	30	20	10	.09	2,900	<2
9/11/97	9.5	310	<1	<10	.7	44	6	56	15	<2	<4	<8	<4	25	19	12	.11	2,300	<2
9/23/98	10	300	.75	<1	.57	31	5.2	42	13	<1	5.7	<1	<1	18	17	10	.1	1,600	.52
<b>Wolf River at Keshena, Wis., station 4077100</b>																			
9/25/96	11	350	<1	<10	.7	55	8	55	13	<2	9	<8	<4	32	26	10	.08	2,800	<2
9/11/97	11	350	<1	<10	.7	58	7	59	18	<2	<4	<8	<4	31	23	13	.09	3,400	<2
9/23/98	17	340	.81	<1	.56	47	5.5	45	14	<1	5.8	<1	<1	27	23	11	.1	3,500	.5

Date	Element concentration (micrograms per gram dry weight)																	
	Neodymium	Nickel	Niobium	Scandium	Selenium	Silicon	Silver	Strontium	Tantalum	Thallium	Thorium	Tin	Titanium	Uranium	Vanadium	Yttrium	Ytterbium	Zinc
<b>Wolf River at Highway M near Langlade, Wis., station 4075050</b>																		
10/26/95	16	12	8	6	1.9	0.3	0.2	87	<40	<5.8	<5	0.18	4.06	52	16	2	99	
9/23/96	25	11	8	7	1.8	.4	.2	83	<40	10	<5	.2	4.48	60	22	2	87	
9/11/97	22	10	5	5	1.7	.31	.2	74	<40	11	<5	.18	4.71	57	19	2	86	
9/23/98	16	9.4	4.2	4.9	1.7	.18	.71	63	<1	<1	3.6	1.4	.13	2.8	42	14	1.3	77
<b>Wolf River at Keshena, Wis., station 4077100</b>																		
9/25/96	24	12	8	6	1.6	.4	.2	81	<40	9.4	<5	.2	3.55	54	22	2	83	
9/11/97	27	11	<4	6	1.8	.28	.2	79	<40	11	<5	.19	3.11	57	22	2	89	
9/23/98	22	9.6	4.9	4.8	1.8	.16	.44	70	<1	<1	4.9	1.8	.14	2.4	43	18	1.7	82

**Appendix 7.** Concentrations of major ions and carbon in fine streambed sediment (less than 0.062 mm) from sites on the Wolf River in the vicinity of the Menominee Indian Reservation

Date	Element concentration (percent)										
	Aluminum	Calcium	Iron	Magnesium	Phosphorus	Potassium	Sodium	Sulfur	Carbon, organic	Carbon, inorganic	Carbon, organic and inorganic
10/26/95	3	1.5	2.6	0.53	0.17	0.95	0.53	0.38	13.7	0.1	13.8
9/23/96	3	1.9	3.2	.74	.19	.93	.59	.28	13	.26	13.3
9/11/97	2.6	1.6	2.7	.57	.2	.88	.48	.31	14.3	.18	14.5
9/23/98	2.6	1.6	2.3	.58	.17	.85	.43	.34	12.8	.17	13
<b>Wolf River at Highway M near Langlade, Wis., station 4075050</b>											
<b>Wolf River at Keshena, Wis., station 4077100</b>											
9/25/96	2.8	1.9	3	.73	.19	.79	.56	.29	11.6	.26	11.9
9/11/97	2.7	1.8	2.9	.71	.23	.98	.51	.32	13.2	.28	13.5
9/23/98	2.3	1.9	2.7	.66	.22	.8	.37	.37	13.5	.31	13.8

**Appendix 8.** Concentrations of elements in biota from sites on the Wolf River in the vicinity of the Menominee Indian Reservation

Date	Biota type	Water (percent)	Element concentration (micrograms per gram dry weight)						
			Aluminum	Antimony	Arsenic	Barium	Beryllium	Boron	Cadmium
<b>Wolf River at Highway M near Langlade, Wis., station 4075050</b>									
10/25/95	White sucker	76.4	<1.0	<0.20	0.40	0.10	<0.20	1.6	<0.20
9/23/96	White sucker	81.3	<1.0	<20	.30	<1.0	<20	.30	<20
9/11/97	White sucker	83.4	1.10	<48	<48	.206	<48	1.0	<48
9/23/98	White sucker	80.4	2.58	<26	.35	4.77	<26	.58	<26
10/25/95	Caddisfly larvae	82.3	257	<30	1.7	24.0	<30	3.0	<30
9/23/96	Caddisfly larvae	84.1	367	<20	1.5	50.6	<20	2.2	<20
9/11/97	Caddisfly larvae	78.9	236	<22	1.34	17.4	<22	3.2	<22
9/22/98	Caddisfly larvae	84.0	249	<33	2.03	47.1	<33	4.6	<33
<b>Wolf River at Keshena, Wis., station 4077100</b>									
9/24/96	White sucker	81.9	10.6	<40	.4	.60	<40	.80	<40
9/10/97	White sucker	81.8	<19	<38	<38	.11	<38	.53	<38
9/23/98	White sucker	80.7	<1.0	<27	.48	3.72	<27	.57	<27
9/24/96	Caddisfly larvae	84.4	161	<30	1.2	44.3	<30	1.9	<30
9/11/97	Caddisfly larvae	85.6	320	<78	1.51	67.8	<78	3.9	<78
9/22/98	Caddisfly larvae	84.5	283	<32	1.65	65.3	<32	3.4	<32

Date	Biota type	Water (percent)	Element concentration (micrograms per gram dry weight)						
			Chromium	Cobalt	Copper	Iron	Lead	Manganese	Mercury
<b>Wolf River at Highway M near Langlade, Wis., station 4075050</b>									
10/25/95	White sucker	76.4	0.70	<0.20	25.7	224	<0.20	6.70	<0.10
9/23/96	White sucker	81.3	.80	<20	28.3	460	<20	6.60	<08
9/11/97	White sucker	83.4	.67	<48	4.11	716	<48	4.46	<01
9/23/98	White sucker	80.4	.59	<26	16.7	518	<26	7.97	.06
10/25/95	Caddisfly larvae	82.3	1.8	.40	9.90	1,070	.80	634	<10
9/23/96	Caddisfly larvae	84.1	2.4	.50	10.5	1,400	.90	707	<04
9/11/97	Caddisfly larvae	78.9	1.9	.31	10.5	1,030	.48	1,220	.02
9/22/98	Caddisfly larvae	84.0	2.4	.47	13.4	1,100	.98	1,890	.07
<b>Wolf River at Keshena, Wis., station 4077100</b>									
9/24/96	White sucker	81.9	1.0	<40	16.8	670	<40	31.4	<07
9/10/97	White sucker	81.8	.67	<38	59.3	715	<38	18.2	.01
9/23/98	White sucker	80.7	.61	<27	58.0	887	<27	9.08	.40
9/24/96	Caddisfly larvae	84.4	1.9	.30	9.80	866	.70	823	<04
9/11/97	Caddisfly larvae	85.6	2.5	<78	13.0	1,290	.88	939	<01
9/22/98	Caddisfly larvae	84.5	2.3	.39	11.5	1,060	.94	1240	.04

**Appendix 8. Concentrations of elements in biota from sites on the Wolf River in the vicinity of the Menominee Indian Reservation—Continued**

Date	Biota type	Water (percent)	Element concentration (microgram per gram dry weight)									
			Molybdenum	Nickel	Selenium	Silver	Strontium	Uranium	Vanadium	Zinc		
<b>Wolf River at Highway M near Langlade, Wis., station 4075050</b>												
10/25/95	White sucker	76.4	0.70	<0.20	3.5	0.30	<0.10	<0.20	<0.20	<0.20	<0.20	71.7
9/23/96	White sucker	81.3	.70	<20	3.7	.40	<10	<20	<20	<20	.20	88.9
9/11/97	White sucker	83.4	<.48	<.48	2.5	<.48	.155	<.48	<.48	<.48	<.48	58.4
9/23/98	White sucker	80.4	.50	<.26	3.4	<.26	8.14	<.26	<.26	<.26	.41	86.1
10/25/95	Caddisfly larvae	82.3	1.6	.60	.90	<.30	.90	<.30	<.30	<.30	2.1	88.3
9/23/96	Caddisfly larvae	84.1	1.2	.60	.30	<.20	1.3	<.20	<.20	<.20	2.5	99.8
9/11/97	Caddisfly larvae	78.9	1.6	.33	.67	<.22	1.35	.31	.31	1.5	1.5	108
9/22/98	Caddisfly larvae	84.0	1.8	.54	1.2	<.33	1.59	<.33	<.33	2.4	2.4	136
<b>Wolf River at Keshena, Wis., station 4077100</b>												
9/24/96	White sucker	81.9	.50	<.40	4.0	<.40	.40	<.40	<.40	<.40	.50	74.3
9/10/97	White sucker	81.8	.90	<.38	3.7	.50	.123	<.38	<.38	<.38	<.38	113
9/23/98	White sucker	80.7	.96	<.27	5.2	.44	9.06	<.27	<.27	<.27	.64	145
9/24/96	Caddisfly larvae	84.4	1.5	.40	.80	<.30	1.10	<.30	<.30	<.30	1.4	111
9/11/97	Caddisfly larvae	85.6	1.9	<.78	<.78	<.78	1.41	<.78	<.78	<.78	2.0	142
9/22/98	Caddisfly larvae	84.5	1.5	.52	1.0	<.32	1.36	<.32	<.32	<.32	2.4	123

**Appendix 9. Invertebrate taxa of the Wolf River at Keshena and near Langlade, Wis., during 1998**

Phylum	Class	Order	Family	Genus	Species	Keshena	Langlade	
Arthropoda	Insecta (Insects)	Plecoptera (Stoneflies)	Perlidae	**	**	X	X	
				<i>Agnetina</i>	sp.	X		
				<i>Agnetina</i>	<i>capitata</i>	X		
				Pteronarcyidae	<i>Pteronarcys</i>	sp.	X	X
					**	**		X
					**	**	X	X
					<i>Baetis</i>	sp.	X	
					<i>Baetis</i>	<i>intercalaris</i>	X	
					<i>Baetis</i>	<i>flavistriga</i>	X	X
				Baetidae	<i>Baetis</i>	<i>dubius</i>	X	
					<i>Baetis</i>	<i>punctiventris</i>		X
					<i>Acentrella</i>	<i>carolina</i>		X
			<i>Acerpenna</i>		<i>pygmaea</i>	X		
			<i>Caenis</i>		sp.	X		
			**		**	X		
			<i>Ephemerella</i>		sp.	X	X	
			<i>Serratella</i>		<i>deficiens</i>	X	X	
			**		**	X	X	
			Heptageniidae	<i>Epeorus</i>	<i>vitreus</i>	X	X	
				<i>Leucrocuta</i>	<i>hebe</i>		X	
				<i>Rhithrogena</i>	sp.	X		
				<i>Stenonema</i>	sp.	X	X	
				<i>Stenonema</i>	<i>mediopunctatum</i>	X		
				<i>Stenonema</i>	<i>modestum</i>	X		
				Isonychiidae	<i>Isonychia</i>	sp.	X	X
					Leptophlebiidae	<i>Leptophlebia</i>	sp.	

Appendix 9. Invertebrate taxa of the Wolf River at Keshena and near Langlade, Wis., during 1998—Continued

Phylum	Class	Order	Family	Genus	Species	Keshena	Langlade		
Arthropoda	Insecta (Insects)	Odonata (Dragonflies and Damselflies)	Gomphidae	**	**	X	X		
				<i>Ophiogomphus</i>	sp.		X		
			Trichoptera (Caddisflies)	Brachycentridae		<i>Brachycentrus</i>	<i>numerosus</i>		X
						<i>Micrasema</i>	sp.	X	X
					<i>Micrasema</i>	<i>rusticum</i>	X	X	
				Glossomatidae		<i>Protophila</i>	sp.	X	X
						<i>Helicopsyche</i>	<i>borealis</i>	X	X
			Hydropsychidae		**	**	X	X	
			Hydropsychidae		<i>Cheumatopsyche</i>	sp.	X	X	
					<i>Hydropsyche</i>	sp.		X	
					<i>Hydropsyche</i>	<i>phalerata</i>	X		
				<i>Hydropsyche</i>	<i>scalaris</i>	X	X		
				<i>Hydropsyche</i>	<i>valanis</i>		X		
				<i>Macrostemum</i>	<i>zebratum</i>	X			
				<i>Ceratopsyche</i>	sp.	X	X		
				<i>Ceratopsyche</i>	<i>alternans</i>	X			
				<i>Ceratopsyche</i>	<i>morosa bifida</i>	X	X		
				<i>Ceratopsyche</i>	<i>morosa morosa</i>	X	X		
				<i>Ceratopsyche</i>	<i>sparna</i>	X			
		Hydroptilidae			<i>Hydroptila</i>	sp.	X		
					<i>Leucotrichia</i>	<i>pictipes</i>	X	X	
					<i>Lepidostoma</i>	sp.		X	
		Lepidostomatidae	Leptoceridae		**	**	X	X	
	<i>Ceraclea</i>			sp.		X			
Philopotamidae			<i>Oecetis</i>	sp.	X				
			<i>Chimarra</i>	sp.	X	X			
			<i>Chimarra</i>	<i>aterrima</i>		X			

Appendix 9. Invertebrate taxa of the Wolf River at Keshena and near Langlade, Wis., during 1998—Continued

Phylum	Class	Order	Family	Genus	Species	Keshena	Langlade		
Arthropoda	Insecta (Insects)	Trichoptera (Caddisflies)	Philopotamidae	<i>Chimarra</i>	<i>socia</i>	X	X		
			Psychomyiidae	<i>Psychomyia</i>	<i>flavida</i>	X	X		
			Coleoptera (Beetles)	Elmidae	<i>Optioservus</i>	sp.	X	X	
					<i>Optioservus</i>	<i>trivittatus</i>	X	X	
				<i>Stenelmis</i>	sp.	X	X		
				<i>Stenelmis</i>	<i>mera</i>	X			
				Psephenidae	<i>Psephenus</i>	<i>herricki</i>	X	X	
				Diptera (True Flies)	Athericidae	<i>Atherix</i>	<i>variegata</i>	X	X
						**	**	X	X
					Empididae	<i>Hemerodromia</i>	sp.		X
		Simuliidae	<i>Simulium</i>		sp.		X		
			<i>Simulium</i>		<i>fibringflatum</i>	X			
			Tipulidae		<i>Antocha</i>	sp.	X	X	
				<i>Dicranota</i>	sp.	X			
		Chironomidae	Diptera (True Flies)	Chironomidae	<i>Pseudolimnophila</i>	sp.	X	X	
					**	**	X		
				Tanypodinae	**	**	X	X	
					<i>Conchapelopia</i>	sp.	X		
				Orthocladinae	**	**	X		
					<i>pupae</i>		X	X	
<i>Cardiocladius</i>	sp.				X				
<i>Cardiocladius</i>	<i>pupae</i>				X				
<i>Cricotopus</i>	sp.					X			
<i>Cricotopus</i>	<i>bicinctus</i> group				X	X			
Nanocladiinae	<i>Cricotopus</i>	<i>trifascia</i> group	X	X					
	<i>Eukiefferiella</i>	sp.	X						
	<i>Nanocladius</i>	sp.	X						
	<i>Nanocladius</i>	<i>cf. alternantherae</i>	X						

Appendix 9. Invertebrate taxa of the Wolf River at Keshena and near Langlade, Wis., during 1998—Continued

Phylum	Class	Order	Family	Genus	Species	Keshena	Langlade					
Arthropoda	Insecta (Insects)	Diptera (True Flies)	Chironomidae									
								Orthoclaadiinae	<i>Orthoclaadius</i>	sp.	X	
									<i>Synorthoclaadius</i>	sp.	X	
									<i>Thienemanniella</i>	sp.	X	X
									<i>Tvetenia</i>	sp. B	X	X
									**	**	X	X
									<i>Paratanytarsus</i>	sp. A	X	
									<i>Rheotanytarsus</i>	sp.	X	X
									<i>Stempellina</i>	<i>montivaga</i> group	X	X
									<i>Polypeditum</i>	<i>nr. convictum</i>	X	X
			**	**	X							
Nematoda	Arachnoidea (Roundworms)	Acari (Water mites)		**	**	X						
				**	**		X					
Platyhelminthes	Turbellaria	(Flatworms)										
Mollusca	Gastropoda	Limnophila (Limpets)		<i>Laevapex</i>	sp.	X						
				<i>Sphaerium</i>	sp.							
Annelida	Pelecypoda	Veneroidea										
	Oligochaeta (Aquatic earthworms)	Haplotaenida		**	**		X					
	Hirudinea (Leeches)	Pharyngobdellida	Erpobdellidae	**	**		X					

Appendix 10. Algal taxa of the Wolf River near Langlade and at Keshena, Wis., during 1998

Phylum family	Genus	Species	Variety	Authority	Langlade	Keshena
Chlorophycophyta (GREEN ALGAE)						
Chlamydomonadales	<i>Chlamydomonas</i>	sp.				X
Desmidiaceae	<i>Cosmarium</i>	<i>formosulum</i>		Hoffman		X
Oocystaceae	<i>Ankistrodesmus</i>	<i>falcatus</i>		(Corda) Ralfs	X	X
	<i>Selenastrum</i>	sp.			X	
Scenedesmaceae	<i>Scenedesmus</i>	<i>ecornis</i>		(Ralfs) Chod.		X
	<i>Scenedesmus</i>	<i>quadricauda</i>		(Turp.) Bréb.		X
	<i>Scenedesmus</i>	<i>acuminatus</i>		(Lagerh.) Chod.	X	X
Chrysochycophyta (DIATOMS)						
Achnantheaceae						
	<i>Achnanthes</i>	<i>clevelandi</i>		Grun.	X	X
	<i>Achnanthes</i>	<i>deflexa</i>		Reim.	X	X
	<i>Achnanthes</i>	<i>delicatula</i>		(Kütz.) Grun.	X	X
	<i>Achnanthes</i>	<i>exigua</i>	heterovalva	Krasske	X	X
	<i>Achnanthes</i>	<i>lanceolata</i>		(Bréb. in Kütz.) Grun.	X	X
	<i>Achnanthes</i>	<i>lanceolata</i>	omissa	Reim.	X	X
	<i>Achnanthes</i>	<i>lanceolata</i>	rostrata	(Østr.) Lange-Bert.	X	
	<i>Achnanthes</i>	<i>minutissima</i>		Kütz.	X	X
	<i>Achnanthes</i>	<i>pinnata</i>		Hust.		X
	<i>Cocconeis</i>	<i>diminuta</i>		Pant.	X	X
	<i>Cocconeis</i>	<i>placentula</i>	lineata	(Ehr.) V. H.	X	X
	<i>Cocconeis</i>	<i>pediculus</i>		Ehr.	X	X
Diatomaceae						
	<i>Diatoma</i>	<i>vulgare</i>		Bory	X	X
	<i>Fragilaria</i>	<i>brevistriata</i>		L-Bert.	X	X
	<i>Fragilaria</i>	<i>brevistriata</i>	inflata	(Pant.) Hust.		X
	<i>Fragilaria</i>	<i>capucina</i>	mesolepta	Rabh.	X	X
	<i>Fragilaria</i>	<i>construens</i>		(Ehr.) Grun.	X	X
	<i>Fragilaria</i>	<i>construens</i>	pumila	Grun.		X

Appendix 10. Algal taxa of the Wolf River near Langlade and at Keshena, Wis., during 1998—Continued

Phylum family	Genus	Species	Variety	Authority	Langlade	Keshena
Chrysiophycephyta (DIATOMS)	Diatomaceae	<i>Fragilaria</i>	<i>pinnata</i>	Ehr.	X	X
		<i>Fragilaria</i>	<i>leptostauron</i>	(Ehr.) Hust.	X	X
		<i>Fragilaria</i>	<i>vaucheriae</i>	(Kütz.) Peters.		X
		<i>Opephora</i>	<i>olsenii</i>	M Moller		X
		<i>Opephora</i>	<i>martyi</i>	Hérib.	X	
		<i>Synedra</i>	<i>rumpens</i>	Kütz.		X
		<i>Synedra</i>	<i>parasitica</i>	(Grun.) Hust.		X
		<i>Synedra</i>	<i>ulna</i>	(Hérib.) Hust.	X	X
		<i>Synedra</i>	<i>ulna</i>	(Nitz.) Ehr.	X	X
		<i>Melosira</i>	<i>varians</i>	Ag.	X	
		<i>Amphora</i>	<i>perpusilla</i>	(Grun.) Grun.		X
		<i>Amphora</i>	<i>ovalis</i>	(Kütz.) V. H. ex DeT.		X
		<i>Cymbella</i>	<i>affinis</i>	Kütz.	X	
		<i>Cymbella</i>	<i>minuta</i>	Hilse ex Rabh.	X	X
		<i>Cymbella</i>	<i>prostrata</i>	(Rabh.) Reim.	X	
		<i>Cymbella</i>	<i>proxima</i>	Reim.	X	X
		<i>Cymbella</i>	<i>reichardtii</i>	Kram.	X	
<i>Cymbella</i>	<i>tumida</i>	(Bréb. ex Kütz.) V. H.	X	X		
<i>Cymbella</i>	<i>turgidula</i>	Grun.	X	X		
<i>Gomphonema</i>	<i>apuncto</i>	Wallace	X			
<i>Gomphonema</i>	<i>intricatum</i>	Grun. in V.H.		X		
<i>Gomphonema</i>	<i>parvulum</i>	(Kütz.) Kütz.	X	X		
<i>Gomphonema</i>	<i>spaeerophorum</i>	Ehr.		X		
<i>Navicula</i>	<i>cryptocephala</i>	Kütz.		X		
<i>Navicula</i>	<i>cryptocephala</i>	(Kütz.) Rabh.	X			
<i>Navicula</i>	<i>decussis</i>	Østr.		X		
<i>Navicula</i>	<i>gastrum</i>	(Ehr.) Kütz.	X			

Appendix 10. Algal taxa of the Wolf River near Langlade and at Keshena, Wis., during 1998—Continued

Phylum family	Genus	Species	Variety	Authority	Langlade	Keshena
Chrysophyophyta (DIATOMS)						
Naviculaceae	<i>Navicula</i>	<i>lanceolata</i>		(Ag.) Kütz.	X	
	<i>Navicula</i>	<i>menisculus</i>		Schumm.		X
	<i>Navicula</i>	<i>minima</i>		Grun.	X	X
	<i>Navicula</i>	<i>pupula</i>		Kütz.		X
	<i>Navicula</i>	<i>radiosa</i>	<i>tenella</i>	(Bréb. ex Kütz.) Grun.	X	X
	<i>Navicula</i>	<i>salinarum</i>	<i>intermedia</i>	(Grun.) Cl.	X	X
	<i>Navicula</i>	<i>scutelloides</i>		W. Sm. ex Greg.	X	X
	<i>Navicula</i>	<i>tripunctata</i>		(O. F. Müll.) Bory	X	X
	<i>Reimeria</i>	<i>sinuata</i>		(Greg.) Kociolek & Stoermer	X	X
	<i>Nitzschia</i>	<i>amphibia</i>		Grun.		X
Nitzschiaceae	<i>Nitzschia</i>	<i>fonticola</i>		Grun.	X	
	<i>Nitzschia</i>	<i>frustulum</i>		(Kütz.) Grun.		X
	<i>Nitzschia</i>	<i>inconspicua</i>		Grun.	X	
	<i>Nitzschia</i>	<i>linearis</i>		(Ag. ex W. Sm.) W. Sm.		X
	<i>Nitzschia</i>	<i>sigmoidea</i>		(Nitz.) W. Sm.	X	
	<i>Cyclotella</i>	<i>meneghiniana</i>		Kütz.		X
Cyanochloronta (BLUE-GREEN ALGAE)						
Chroococcaceae	<i>Merismopedia</i>	<i>glauc</i>		(Ehr.) Naeg.	X	
	<i>Calothrix</i>	<i>parietina</i>		(Naeg.) Thuret	X	X
Oscillatoriaceae	<i>Hydrocoleum</i>	<i>breissonii</i>		Kütz.	X	
	<i>Lyngbya</i>	sp. 1 ANS FWA		X		X
	<i>Oscillatoria</i>	sp.		X		
	<i>Oscillatoria</i>	sp. 1 ANS FWA		X		X
	<i>Oscillatoria</i>	<i>lutea</i>		Ag.	X	
Rhodophyophyta (RED ALGAE)						
Chantransiacea	<i>Audouinella</i>	<i>violacea</i>		Kütz.	X	